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A review of bio-oils from waste biomass: Focus on fish processing waste

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A B S T R A C T

Biofuels are derived from biomass using biochemical, thermochemical, and physical and chemical extraction processes. Waste oils from animal and vegetable sources continue to be important biomass feedstock due to the potential benefits over petroleum and some of the virgin vegetable oil based fuels. In this paper, the chemical, thermal, and physical properties of biofuels derived from virgin and waste sources are reviewed. In addition, the processes used for recovering bio-oils from animal fats (beef tallow, lard, and poultry waste) and greases, and purification and refining of bio-oils are discussed as well as the resulting performance as a fuel. Particular focus will be on production of biofuels from fish waste. The potential for biofuel from fish waste is a function of the location and size of the processing plant, type of fuel requirements, and characteristics of the fish waste.

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1. Introduction

Plant matter, animal waste, agricultural crops and residues, municipal waste, and industrial effluents are all possible feedstock for deriving biofuels [1–3]. Bio-gas, bio-oil and bio-char are typically converted from biomass via biochemical, thermochemical, physical, and/or chemical processes [3,4]. Fig. 1 outlines possible biofuels and potential end use. Bio-gases are produced via gasification, pyrolysis and anaerobic digestion [3–5]. Partial gasification with steam or CO_2 or a mixture of both, pyrolysis, and chemical activation processes are used for bio-char production [5]. Bio-oils are produced using pyrolysis, fermentation, hydrolysis and physical/chemical extraction and conversion processes [4,6].

Bio-oils are derived from biomass such as edible and non edible oilseed crops, wood (lignocelluloses), microorganisms, algae, animal waste, and recycled cooking greases [2,7]. Rapeseed, soybean, palm, sunflower, corn, safflower, canola, mustard, jatropha and mahua are the most common virgin crops for bio-oil production [7–10]. Corn, wheat, rice straw, sugar cane/beet and sweet sorghum are used for bio-ethanol production [1]. However, the food vs. fuel debate and other environmental impacts related to cultivation and conversion can limit the use of food crops for fuel. Utilization of unproductive land and low quality edible oils produced for human food consumption and growth as a rotation crop address some of the issues [7]. The conversion of residues from wood or lignocellulosic material to biofuels is difficult, and advanced technologies are expected to reach their commercial stage in the next decades [11]. Yeast, bacteria, algae, and fungi do not require land for production, and the lipid content of yeast can be up to 70% [2]. However, large scale oil production is challenging with both microalgae and microorganisms [2]. Biofuels from waste biomass have the advantage of recovering a valuable by-product from a waste stream thereby decreasing the volume of waste and toxicity.

Waste biomass associated with the food industry includes yellow grease, brown grease, beef tallow, meat and poultry waste, and fish waste [7]. Yellow grease is waste oil from restaurants using deep frying oils and is used as an animal feed, limiting its use as a fuel. Brown grease from restaurant grease traps is high in contaminants and degraded products; requiring treatment through several mechanical, thermal and chemical treatment processes and limiting potential energy benefits in its use as a fuel. By-products from poultry and fish processing industries are also utilized for producing fats and oils in addition to protein meals. Beef tallow is a by-product of cattle slaughter plants [12]. Bovine spongiform encephalopathy has limited the use of beef tallow for other uses, therefore, both chemical conversion to bio-oils and direct firing, are options. One of the key parameters in use as a fuel is the type of biofuel produced. In the proceeding sections the focus is on bio-oils.

1.1. Composition of bio-oils

Fats and oils derived from biomass are known as lipids, and include fatty acids, their derivatives, and substances related to their compounds [13]. Although classes of lipids are common to all species, the fatty acid composition is a function of the origin (plant, animal, aquatic species or microbial). Relevant lipid classes related to bio-oils include triacylglycerols (TAG) and related compounds (diacylglycerols, monoacylglycerols), hydrocarbons (HC), ketones (KET), alcohols (ALC), cholesterol, sterols (ST), wax esters (WE), FFA, glycero-phospholipids, glycerol-glycolipids, etherlipids and sphingolipids [13,14].

Triacylglycerols (TAG) are the key lipid fraction of interest in the use of bio-oil as a fuel. A TAG comprised of three fatty acids with a glycerol molecule (Fig. 4). TAG and other lipid molecules decompose and form FFA and high FFA levels (>5%) limit waste fat/oil use as a fuel [2]. For instance, recycled oils and animal fats have up to 15–20% FFA content, due to decomposition in processing [2,7]. Refined canola and soybean oil have FFA less than 1.5% while greases and animal fats can range from 1.5% to over 20%; specifically yellow grease has less than 15% FFA while brown grease levels are typically greater than 15% [7,15]. Some virgin vegetable oils also have high FFA, for instance, mahua oil has a FFA of 20% [8].

Fatty acids (FA) constitute a major part of TAG molecule in bio-oils and can be 94–96 wt.% [15]. Fuel properties of bio-oils vary depending on the FA carbon chain length, degree of saturation of the carbon bonds, and the number of unsaturated carbon bonds of the fatty acids. The degree of saturation determines the category of FA; saturated fatty acids (SFA), monounsaturated fatty acids

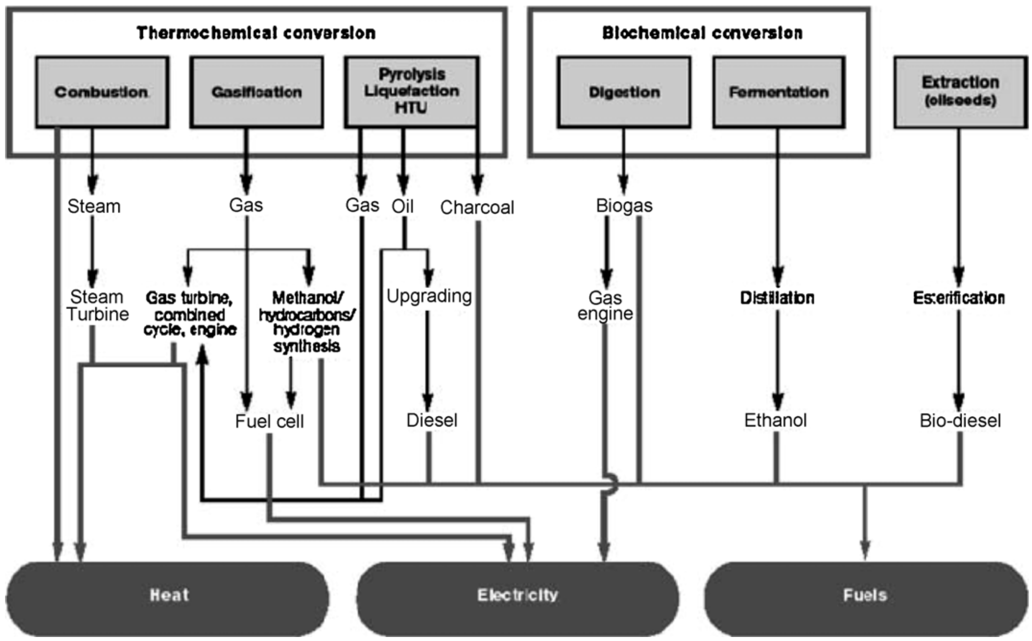


Fig. 1. Biomass conversion processes and products [4].

(MUFA), and polyunsaturated fatty acids (PUFA) [2]. Saturated fatty acids have single bonds, MUFA contain one double bond, and PUFA have multiple (>1) double bonds. Table 1 outlines the structure of FA indicating the number of carbons and degree of saturation (e.g. C12:1 has 12 carbon atoms with one unsaturated bond) and the omega sign indicates the position of the double bond.

Fats contain high SFA compared to oils and are solids at room temperature [17]. The recovered or waste bio-oils (or liquids) range from C6 to C26 [2]. As indicated in Table 2, the predominant fatty acids present in the waste oils are MUFA in the C16–C18 range, while vegetable based oils tend to be higher in C16:0, C18:0, C18:1 and C18:2 [2]. When compared to vegetable oils, waste oils have higher ratios of SFA to Unsaturated fatty acids [2,19,20].

Table 1
Systematic and trivial names and structures of fatty acids [2,10,16–18].

Structure	Trivial name	Systematic name	Formula
C12:0	Lauric	Dodecanoic	$C_{12}H_{24}O_2$
C14:0	Myristic	Tetradecanoic	$C_{14}H_{28}O_2$
C14:1	Myristoleic	Tetradecenoic	$C_{14}H_{26}O_2$
C15:0		Pentadecanoic	$C_{15}H_{30}O_2$
C15:1		Pentadecenoic	$C_{15}H_{28}O_2$
C16:0	Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$
C16:1	Palmitoleic	9-Hexadecanoic	$C_{16}H_{30}O_2$
C17:0	Margaric	Heptadecanoic	$C_{17}H_{34}O_2$
C17:1		Heptadecenoic	$C_{17}H_{32}O_2$
C18:0	Stearic	Octadecanoic	$C_{18}H_{36}O_2$
C18:1omega9	Oleic	9-Octadecenoic	$C_{18}H_{34}O_2$
C18:2omega6	Linoleic	9,12-Octadecadienoic	$C_{18}H_{32}O_2$
C18:3omega6	γ-Linolenic	6,9,12-Octadecatrienoic	$C_{18}H_{30}O_2$
C18:3omega3	α-Linolenic	9,12,15-Octadecadienoic	$C_{18}H_{30}O_2$
C20:0	Arachidic	Eicosanoic	$C_{20}H_{40}O_2$
C20:1	Gadoleic	Eicosenoic	$C_{20}H_{38}O_2$
C20:2		Eicosadienoic	$C_{20}H_{36}O_2$
C20:3omega3		Eicosatrienoic	$C_{20}H_{34}O_2$
C20:3omega6	Dihomo-γ-Linolenic	8,11,14-Eicosatrienoic	$C_{20}H_{34}O_2$
C20:4omega6	Arachidonic	5,8,11,14-Eicosatetraenoic	$C_{20}H_{32}O_2$
C20:5omega3	Clupanodonic (EPA)	5,8,11,14,17-Eicosapentaenoic	$C_{20}H_{30}O_2$
C21:0			$C_{21}H_{42}O_2$
C22:0	Behenic	Docosanoic	$C_{22}H_{44}O_2$
C22:1omega9	Erucic	Docosenoic	$C_{22}H_{42}O_2$
C22:2	Brassic	Docosadienoic	$C_{22}H_{40}O_2$
C22:6omega3	DHA	4,7,10,13,16,19-Decosahexaenoic	$C_{22}H_{32}O_2$
C23:0			$C_{23}H_{46}O_2$
C24:0	Lignoceric	Tetracosanoic	$C_{24}H_{48}O_2$
C24:1	Nervonic	Cis-tetracosenoic	$C_{24}H_{46}O_2$

1.2. Fuel properties

The source and composition of bio-oils directly impact the qualities of the fuel. The key biofuel parameters include viscosity, density, flash point, oxidation stability, and thermal properties. Viscosity is a critical factor for the engine performance with respect to flow of oil through flow lines, orifices and injector nozzles [10]. As viscosity increases, pump pressures increase, fuel atomization is reduced and incomplete or early combustion can occur due to high line pressure [15]. Viscosity increases with the number of carbon atoms and decreases with unsaturated bonds, thus, waste oils have higher viscosities than vegetable oils.

Density affects the break up of fuels injected in engine cylinders [15]. As density increases, compression ratio, amount of fuel injected in terms of mass (for the same fuel volume of input) and the diameter of the fuel droplets increase, directly impacting injection timing and injection spray patterns. Heating value and the engine exhaust emissions are also functions of density. Higher density fuels decrease atomization and mixing, and are associated with higher PM and NO_x emissions than low density fuels. Density increases with the number of carbon atoms and the degree of saturation. Waste oils have higher densities than vegetable oils due to higher SFA content.

Flash point indicates the presence of highly volatile and flammable substances in fuels [10]. Bio-oils generally have higher flash points compared to mineral diesel oils, while flash points of animal fats are higher than vegetable oils due to higher SFA [10,15]. Fuels with high flash points have lower volatilities, cause delayed ignition and difficulties in engine start up.

Fatty acids in bio-oils are oxidized to form products such as peroxides, which is represented by a gain in mass [21]. Due to the presence of unsaturated fatty acids and water in waste oils, lipids can be subjected to lipolysis (enzymatic hydrolysis) and oxidation [22]. Several different indicators are used to measure oxidation; FFA content is a basic indicator. Peroxide value measures primary

Table 2
Fatty acid composition of bio-oil feedstock by wt.%.

Source oil	C16:0	C16:1	C18:0	C18:1	C18:2	C20:0C22:0	C20:1C22:1	SFA	MUFA	PUFA
Yellow grease	23	1	10	**50**	15	–	–	34	51	15
Tallow	25–30	2–3	21–26	**39–42**	2	0.4–1	0.3	49–60	41–45	2
Lard	25–30	2–5	12–16	**41–51**	4–22	–	2–3	38–46	45–59	4–22
Palm	32–47	–	1–6	**40–52**	2–11	–	–	34–59	40–52	2–11
Corn	1–2	1–4	30–50	**34–56**	–	0–2	–	39–64	35–60	
Sunflower	6.0	–	4.2	18.7	**69.3**	1.4	–	11.6	19	69.6
Soybean	7–11	0–1	3–6	22–34	**50–60**	5–10	–	15–27	22–35	52–70
Rapeseed	2–5	0.2	1–2	10–15	10–20	0.9	50–60	4–7	60–75	15–30

Modified from [2].
Bold: Highest type/amount of fatty acid.

Table 3
Effect of fatty acid classes on fuel properties [2].

	Higher SFA	Higher MUFA	Higher PUFA
Freezing point	High	Moderate	Low
Oxidation stability	High	Moderate	Low
Cetane number	High	Moderate	Low
NO_x emissions	Low	Moderate	High

oxidation products, and "ansidine value" is a measure of secondary products. Total oxidation or totox value combines ansidine and peroxide values [23].

Thermal properties such as melting/freezing, crystallization, enthalpy and specific heat capacity, and reactions such as thermal oxidation and decomposition impact fuel properties [21]. Thermal stability measures the changes in weight due to thermal oxidation and/or decomposition. Constituents of bio-oils such as lipids, water and other impurities, aging and amount of heat treatment the oil was subjected to affect freezing and melting points [21,24]. High levels of SFA (30–60 wt.%) in waste oils result in greater than 0 °C melting or freezing points [24]. Melting points below 0 °C occur when unsaturated fatty acids are present and further decrease with the number of double bonds.

Pour point, cloud point, cold filter plugging point (CFPP) as well as freezing point are critical in determining the cold temperature performance of a fuel [10]. Pour point defines the lowest temperature at which a fuel can be pumped or poured [15]. Cloud point measures the temperature at which a wax appears. Fats and oils derived from biological feedstock tend to have low cold temperature properties. Bio-oils from animal fats and greases have poor cold flow than vegetable oils, due to higher SFA content [15,17]. For example beef tallow has about 50 wt.% of SFA making cloud and pour points to occur at higher temperatures than vegetable oils [17].

Cetane number correlates to both specific gravity and distillation temperatures of diesel fuels [10]. Fuels with high cetane numbers such as diesel oil cause lower ignition delays and particulate emissions. Cetane number increases with chain length and level of saturation, and decreases with branching [10,15]. Bio-oils derived from greases and animal fats have higher cetane numbers. Relative effect of fatty acid classes on the fuel properties is summarized in Table 3. Fuels with higher MUFA have better overall properties compared to fuels with higher SFA and PUFA [2].

Various studies [1–3,10] discuss bio-oil refining related to the virgin vegetable oils (pyrolysis, transesterification, microemulsification) and fuel properties of virgin vegetable based biodiesel. Few have conducted a comprehensive discussion on up-stream processes such as recovery and purification including the fuel properties and emissions from crude/purified waste derived bio-oils [7,12,15,19,20] and other forms of converted/refined bio-oils (other than biodiesel). There are limited published studies specifically related to the production of liquid biofuels from fish processing plant waste. Therefore, this review aims to first provide a general overview on recovery, purification and refining methods and the related fuel properties of bio-oils from waste biomass feedstock and some virgin vegetable oils (Section 2), and secondly, discuss the specifics on biofuels from fish processing plant waste (Section 3). Section 3 provides an integrated discussion on the composition of fish processing plant waste, typical recovery and purification methods, and the composition, fuel properties and engine performance/emissions of crude and refined bio-oils from fish waste. Section 4 discusses the applicability of biofuels from fish waste in remote fishing communities by using the province of Newfoundland and Labrador (Canada) as a case study.

2. Bio-oils processing and fuel characteristics of products

2.1. Methods of recovery and purification

Bio-oils are recovered from biomass primarily using thermal and extraction processes, however, bio-chemical processes such as fermentation, digestion and hydrolysis are also used [4,25].

2.1.1. Pyrolysis

Pyrolysis of biomass involves the thermal breakdown at high temperatures (350–700 °C) in the absence of oxygen and in some cases in the presence of a catalyst [10,17,26]. Products of biomass pyrolysis include bio-gas, bio-char and bio-oil depending on the pyrolysis system used [5]. Pyrolyzed gas is predominantly CO, CO_2 and methane (CH_4); bio-oil is composed of organic acids, esters, alcohols, ketones, aldehydes, phenols, alkenes, nitrogen compounds, furans, guaiacols, syringols, sugars, miscellaneous oxygenates and inorganic metals, while char is predominantly elemental carbon and hydrogen [26]. The degree of pretreatment and operating parameters determines the distribution of products and depending on the type of pyrolysis (conventional/slow, fast or flash) a higher solid or oil fraction is produced [26,27]. Conventional pyrolysis uses low temperatures (400 °C) and higher residence times (higher than 20 s), while fast pyrolysis uses moderate temperatures (500 °C) and shorter retention times (1 s) [28]. Fast pyrolysis also produces higher oil fractions (75 wt.%), compared to conventional pyrolysis. In the process (Fig. 2), the biomass is dried to less than 10% moisture, ground (2 mm for fluidized bed reactors), the pre-treated feed is cracked in the reactor, and the three products (gas, oil and char) are further separated. Rapid heating rates, residence times of few seconds or less are used in flash pyrolysis, where particle size of feed is reduced to 105–250 μm.

Rapeseed cake, sunflower bagasse, hazelnut shell, cottonseed cake, and safflower seed have been processed in conventional and fast pyrolysis [26]. In the study by Chaala et al., pelletized beef and bone meal flour were used to produce 35.1 wt.% of bio-oil through vacuum pyrolysis (conventional pyrolysis under a vacuum) [29]. The product was comprised of gas, solid and aqueous phases. Adebanjo et al. pyrolyzed lard at 600 °C, and produced a bio-oil similar in heating value, cetane number, and specific gravity to that of

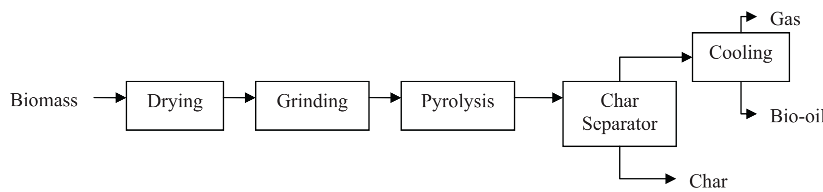


Fig. 2. Fast pyrolysis of biomass feedstock [28].

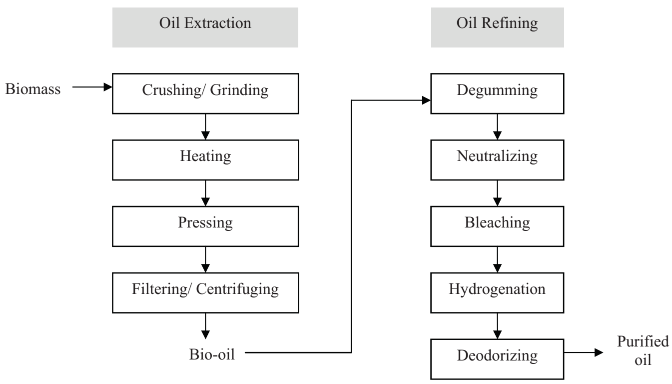


Fig. 3. Process for recovery and chemical refining of bio-oils from biomass [2,24,34].

petroleum diesel [30]. According to the same study, Green Oasis Enviro Economics Inc. used pyrolysis followed by distillation of tallow to obtain bio-oil with distillation curve, flash point (60 °C) and pour point (−28 °C) similar to diesel fuels.

2.1.2. Biological conversion processes

Fermentation (ensilaging) and hydrolysis are biological conversion processes used for recovering oil from waste biomass [31–33]. Hydrolysis is carried out by decomposition of organic matter with the addition of water and enzymes. Fermentation uses bacterial culture and sugar or organic acids to digest organic matter (animal fats) and produce silage, where oil is recovered as a by-product [33].

2.1.3. Extraction

Oil extraction can be done through a physical process involving homogenizing, heating, pressing and filtering as outlined in Fig. 3. For vegetable based biomass the seeds are first crushed, then pressed to squeeze the oil, and filtered [2]. In comparison, oil recovery from yellow grease may only require dewatering and filtering [7]. Mechanical separation methods using heat, filtration and centrifugation are used to remove some of the solid impurities and water from brown grease. Fats and oil from meat products are recovered through rendering (crushing and/or grinding of animal fats followed by cooking at controlled temperatures and mechanical or solvent separation) [2,12]. To prevent hydrolyzing during cooking/heating, water is typically removed; however this has resulted in increasing FFA content [2]. Mechanical separation of oils from the cooked fat is carried out through pressing followed by centrifuging [12]. Supercritical CO_2 extraction is also employed for oil extraction in meat processing [2].

2.1.4. Purification

In addition to TAG, extracted fats and oils still contain sterols (ST), water, FFA, phospholipids (PL), proteins, waxes and gums, pigments and residual solids [34]. Physical and chemical purification methods are used to remove or convert these impurities. Colour compounds, FFA, phosphatides and other minor contaminants are removed through chemical purification, where the oil is degummed, neutralized, bleached, hydrogenated and deodourized as outlined in Fig. 3 [2,24,34].

Water and PL are removed through degumming and neutralizing partially removes the FFA [2,24,34]. The residual FFA, metals, aldehydes, KET, and natural pigments are removed by bleaching, where the oil is mixed with natural or activated clays. Hydrogenation can be used to improve the quality of oil. Deodourizing or stabilizing of odour is achieved through removal of volatile compounds by vacuum steam distillation.

Membranes that are selective to TAG have been proposed and offer simplicity in use and lower cost [35–39]. Separation occurs through molecular size, where the molecular mass distribution of lipid classes are in the ranges of 250–300 kDa for FFA, 550–650 kDa for diglycerides, 750–850 kDa for TAG, 600–800 kDa for PL, and greater than 950 kDa for polymer gums [39]. Membranes used in impurity removal of bio-oils are summarized in Table 4. The use of non porous membranes (composite, polymeric and hydrophobic) has shown to be effective in removal of several contaminants [35,36]. For example, membranes with silicone as the active layer and polyimide as the support layer have removed oxidation products, polar compounds, PL, and moisture. A comparison of advantages and disadvantages of several physical and chemical bio-oil refining processes is given in Table 5.

2.2. Engine performance of crude bio-oils

Crude bio-oils have a number of positive properties compared to petroleum fuels such as high heat content, lower processing requirements and overall lower impacts environmentally, however, they tend to have poor cold flow properties, high viscosity, low volatility, high reactivity (due to high levels of unsaturated carbon chains) [43].

Direct use in engines can be difficult due to polymerization reactions forming gums, and causing carbon deposits and lubricating

Table 4
Membrane pore sizes and their selectivity of membranes [38,40–42].

Purpose/selectivity	Type of membrane	Membrane material	Pore size (μm)	Reference
Dewaxing	Microfiltration	Synthetic polymer	0.02	[41]
Degumming	Ultrafiltration	Polyimide	20 kDa (molecular weight)	[42]
Lipid separation	Microfiltration	Polypropylene coated with mixtures of polymer solutions	0.1	[38]
Dewaxing	Microfiltration		0.2	[41]
Moisture below 0.08 wt.% of animal fats	Microfiltration	Teflon (0.3 MPa pressure)	0.05	[38]
Moisture below 0.08 wt.% of animal fats	Microfiltration	Polyethylene (0.3 MPa pressure)	0.03	[38]
Extremely fine precipitated proteins	Microfiltration	Glass microfiber filter	0.7	[40]
PL	Nanofiltration		4 nm	[38]

Table 5
Advantages and disadvantages of crude bio-oil refining processes [35,36].

Method	Advantages	Disadvantages	References
Active filtration using adsorbents	- Removes particulates - Reduced energy use - Reduced clean up and costs	- Changes the chemistry of the oil - High capital costs - Lack of proper filtration equipment - Can leach foreign matter to the oil	[35]
Distillation	- Improves product yield - Reduced effluent volumes	- Requires higher pretreatment - High energy consumption - Affects the stability of oil	[36]
Chemical purification (Fig. 3)	- Removes sediments and proteins - Reduced viscosity	- High energy consumption - Pollutes the effluent streams - Large use of water and chemicals - Can destroy natural antioxidants	[36]
Membrane separation	- Low energy use - Operates at low temperatures and pressures - No use of chemicals/solvents - Reduces oxidation products, water and sediments, in oil - Retains natural antioxidants	- Lower flux - Can affect oxidation stability - High capital cost	[35]

oil thickening [25,44]. Engine deposits may also be attributed to incomplete combustion and partial vapourization of crude bio-oils due to their high viscosity and low volatility [44]. The composition of some oils can slow gum formation; for example, winter rapeseed oils contain up to 46.7% erucic acid content, compared to 75–85 wt.% linoleic acid in other oils, reducing gum formation [25]. The PUFA in waste oils from animal fats and greases have lower oxidation stability, enhancing degradation and engine deposits [45]. Even small amounts of PUFA can affect oxidation stability of bio-oils to a much larger extent than those with high SFA or MUFA.

Crude vegetable oil and blends were tested in engines as far back as 1980s, where a diesel fleet was powered with a blend of used filtered cooking oil and 5% biofuel, without issues in engine filter build up or coking [46]. However, lubrication oil contamination occurred due to polymerization of PUFA, thus requiring change of lubricating oil every 4000–5000 miles. In direct-injection engines some vegetable oils and blends showed better results than others; for example, sunflower oil blends did not show favourable results, whereas, safflower oils passed the engine manufacturer's association 200 h test [17]. Most issues associated with direct use of bio-oils and blends occurred over long term. Coking and trumpet formation on the fuel injectors (leading to poor fuel atomization), gelling and contamination of lubricating oils, oil ring sticking and thickening, orifice plugging, and carbon deposits are some of the common issues reported in internal combustion engines [17,44]. Preheating of fuel prior to injection, fuel switching to diesel at partial load operation, partially refining the oils to remove gums, and filtering to reduce particle size (less than 4 μm) are proposed to address some of the above mentioned issues [47].

Crude bio-oils are currently used as blends with No. 2 fuel and No. 6 fuel oil in industrial boilers with minor modifications [2]. They have the capability to replace middle distillate petroleum based fuels; however, refining processes are typically employed to improve fuel properties of bio-oils for use over a wide range of applications. Refining is also necessary to reduce engine deposits, engine durability issues and lubricating oil contamination [48]. Refining processes and implications in engine use of refined biofuels are given in Section 2.4.

2.3. *Refining processes*

In refining, the crude oil is converted to forms with properties similar to conventional fuels. Pyrolysis, microemulsification, hydrocracking and transesterification are the most well studied processes [17,49]. A conventional hydro-processing has been investigated, where an iso-paraffin rich diesel substitute was produced from bio-oils [9]. Dilution is also proposed [10].

2.3.1. *Transesterification*

Transesterification is the most commonly used method for conversion of waste and virgin bio-oils to biodiesel. In this process, TAG are converted to fatty acid alkyl esters by combining the acetyl part of the TAG with the alkyl part of the alcohol, where the glyceride group is replaced with hydroxyls (from the alcohol) to form glycerol as a by-product (Fig. 4) [15,44]. The viscosity of bio-oils reduces as a result, without affecting the cetane number and the heating value. A catalyst is used in the process (acid, base, or enzymes) and is a function of the composition of the crude bio-oil feed [17].

2.3.1.1. Base catalyzed transesterification. Base catalyzed transesterification is used for derivatization of bio-oils with FFA contents lower than 5 wt.% [15,50]. Fig. 4 outlines the global reaction; in

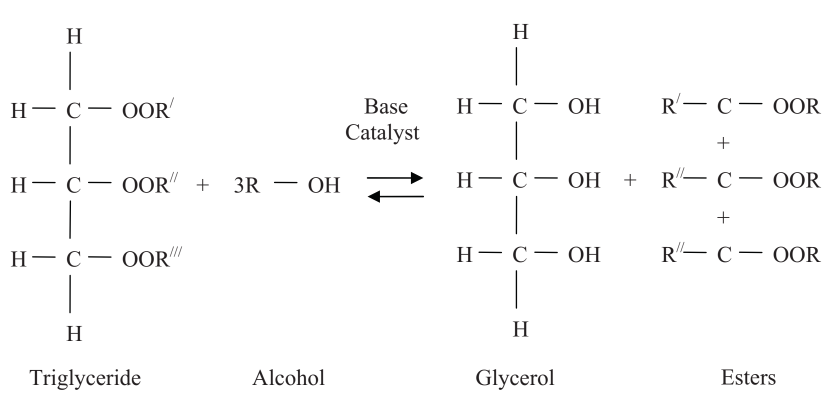


Fig. 4. Base catalyzed transesterification reaction [15].

reality, several reactions take place, where di-glycerides and then mono-glycerides are formed as intermediate products [17].

Methanol, ethanol and branched chain alcohols (such as 2-propanol and 1-butanol) are common alcohols used [15,50]. Ethanol forms stable emulsions making separation of esters difficult, while methanol breaks these emulsions quickly due to the presence of non-polar groups [44]. Methanol also increases the separation and quality of yield and lowers the quantity of alcohol required [44,50]. Methanol/oil ratios between 3:1 and 6:1 have shown higher ester production [51,52]. Conversion efficiencies have ranged between 80% and 99.5% depending on the type of bio-oil [44,53–56]. Cold temperature properties were improved with branched chain alcohols however, branched chain alcohols are higher in cost, require higher molar ratios of alcohol/oil, and form impurities, compared to ethanol or methanol [15,19].

Sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates (e.g. sodium and potassium alkoxides), sodium amide, sodium hydride, potassium hydride and potassium amide are possible base candidates [17,57]. The most commonly used base is NaOH. There are conflicting studies on the effectiveness of sodium methoxide compared to NaOH; for example, NaOH reacted with methanol to produce a small amount of water, while, sodium methoxide formed sodium salts [56,58–60]. The maximum activity of the reaction reached at 0.3 wt.% with NaOH, and 0.5 wt.% with sodium methoxide; therefore NaOH was preferred [44]. Comparison of basic alkaline-earth metal catalysts including; magnesium oxide (MgO), calcium hydroxide ($Ca(OH)_2$), barium hydroxide ($Ba(OH)_2$) and calcium methoxide as substitutes for NaOH in transesterification of rapeseed oil showed NaOH to be more effective in terms of conversion. In addition, NaOH is a low cost chemical relative to other bases, therefore typically used [17].

The presence of water and FFA result in soap formation by partially shifting the transesterification reaction to a saponification reaction, where the TAG react with the base catalyst (e.g. NaOH) to form salt of the fatty acid or soap and glycerol [17,61]. Thus, the feedstock and alcohols need to be anhydrous. Formation of soaps reduces ester yield, requires more catalyst and alcohol, results in separation of products problems (ester, glycerol and wastewater), reduces catalyst efficiency, increases the viscosity of biodiesel, consumes more energy, and increases gel formation [15,62]. To prevent this, bio-oils with higher than 5% FFA content such as in animal fats and grease require pretreatment with an acid [15,17,63].

2.3.1.2. Acid catalyzed pretreatment and base catalyzed transesterification. Pretreatment with acid catalyst followed by base catalyzed transesterification is used for bio-oils with FFA content greater than 5% and in some studies, greater than 0.5% [15,44]. The pretreatment process is outlined in Fig. 5; the FFA are converted to monoesters in the presence of the acid catalyst [15]. Organic sulphonic acid, sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and hydrochloric acid (HCl) are some possible acids [17]. In studies with yellow grease at 12% FFA and brown grease at 33% FFA, the reductions were up to 1% [44].

The lower dispersion of alcohol in bio-oils with high FFA (greater than 5%) will reduce reaction rates and to overcome this higher stirring rates and alcohols concentrations compared to direct catalyzed transesterification are used [15]. Formation of water during the reaction can also inhibit further conversion of FFA to monoesters. The high alcohol use, stir rates and the need to regenerate the alcohol and catalyst result in high energy use. An alternative to the two step process is direct acid catalyzed transesterification where both esterifications are carried out using an acid catalyst. It does not require pretreatment for feedstock with high FFA however, use is limited due to the need for larger reactors, lower reaction rates, high alcohol use and additional corrosion control measures in reactors and engines compared to the two step process.

2.3.1.3. Enzymatic catalysis and alternative transesterification processes. In enzymatic catalyzed transesterification, lipases are used as the catalyst to achieve the same reaction as given in Fig. 4, but with higher conversion [19,57]. For example, Jackson et al. used lipases for methanolysis of corn oil in flowing supercritical CO_2 to achieve conversion efficiency greater than 98% [64]. Lipases are able to completely convert FFA into their alkyl esters (ideal for waste oils and fats), and require minimal processing for removal of glycerol and recovery of esters [44,57]. Lipases also catalyze transesterification in both aqueous and non aqueous mediums [65,66]. However, the popularization of the process is limited due to high costs associated with enzymes [57].

Supercritical methanol/ethanol without the presence of a catalyst has been studied [15,44,67,68]. According to Cao et al., at pressure of 12.8 MPa, temperature of 280 °C, and residence time of 10 min a conversion of 98% was achieved using supercritical methanol [67]. By adding propane as a co-solvent 100% conversion occurred in 5 min, at 300 °C. In a study by Meher et al., complete conversion of SFA to esters at 400 °C was reported using supercritical methanol, while unsaturates completely converted at 350 °C [44]. Pressures used during the process were not given. In another study, simultaneous esterification of FFA and transesterification of TAG were accomplished using supercritical methanol for feedstock with high FFA and water [15]. Use of supercritical ethanol was studied by Madras et al., and 100% conversion occurred at a pressure of 2 MPa, temperature of 350 °C and residence time of 40 min [68]. The high cost due to high temperatures, pressures, alcohol/oil molar ratios (compared to base/acid catalyzed transesterification), and thermal degradation reactions limit application [15,57].

2.3.1.4. Product: composition, recovery and operational issues. Products are made up of esters but by-products that must be removed include glycerol, a mix of di-, tri- and monoglycerides, catalyst, and the alcohol [17,50]. Separation of the ester from the mixture is difficult due to the diglycerides and specifically monoglycerides, as mono-glycerides can cause turbidity in the product mixtures [17,50]. Further mono and diglycerides augment hydrolysis of the ester in the presence of water, natural pro-oxidants (e.g. air), and high temperatures [10]. Glycerol can be separated through gravity separation or centrifuging and sold for commercial use, and the remaining catalyst, soap, salts, methanol and free glycerol are removed by water washing followed by removal of water through a flash vacuum process or distillation [17,57]. Transesterification is typically carried out at near ambient temperatures, as

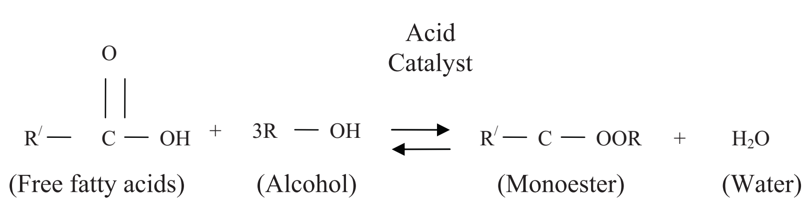


Fig. 5. Acid catalyzed pretreatment esterification reaction.

increasing the temperature has not increased ester conversion efficiency [56,69].

Detection and measurement of the products is the key to determining optimal process conditions, conversion efficiencies, and product quality. Typically, a gas chromatograph (GC) equipped either with mass spectrometry (MS) or flame ionization detectors (FID) is used for simultaneous determination of glycerol, mono, di and tri-glycerides in vegetable methyl esters [44]. GC analysis of products has results that lacked consistency, however the derivatized products (free of hydroxyl groups) have been detected accurately at low concentrations. High performance liquid chromatography (HPLC) has been used in product analysis which reduces analysis time, however, solvents are required as an eluent. Combining HPLC with pulsed amperometric has been used for detection of free glycerol in vegetable oil esters with higher accuracy, and detection of residual alcohol was also possible [70,71]. Other HPLC systems used include reverse phase HPLC with ultra violet detection, evaporative light scattering detection, and atmospheric pressure chemical ionization MS in the determination of products from transesterification of rapeseed oil [72]. For detection of mono, di, and tri-glyceride based methyl esters, an isocratic liquid chromatography with a density detector and solvents has been used with good results [44]. Gel permeation chromatography with a refractive index detector was used for analyzing mono, di, and tri-glycerides, alcohol, glycerol and methyl esters, and sample preparation involved only dilution and neutralization [73]. The balance is choosing analytical system(s) that can detect/measure a range of products from the reaction with low costs and ease of sample preparation.

2.3.2. *Pyrolysis*

Pyrolysis is used for converting vegetable and waste oils to lighter products. Pyrolysis of TAG form, alkanes and alkenes (60%), and alkadienes, aromatics and carboxylic acids (9–16%) [10,17,57,74]. Pyrolysis combined with metallic salt catalysts has been successful in producing paraffins and olefins similar to petroleum based diesel fuels, by using vegetable oils [17]. In other studies, soybean oil has been pyrolyzed to a product with 73–77 wt.% HC, while for safflower oils 80–88 wt.% HC were obtained. Other feedstocks that have been tested include waste fish oil which was fast pyrolyzed after aerobic treatment and centrifugal separation [74]. Challenges in the pyrolysis of waste oils include the high energy intensity and equipment cost and the reduction in oxygenate of the final product [17]. The conversion rates for the pyrolyzed processes are not as reported.

2.3.3. *Microemulsification*

In microemulsification of bio-oils, co-solvents (dispersants) or alcohols and surfactants are added forming thermodynamically stable dispersions of oil, water, surfactant and co-surfactants [10,75]. Solvents that have an affinity to aqueous and non aqueous media are used in the process, such as methanol, ethanol, 2-butanol or other ionic or non-ionic amphiphiles (compounds that have both hydrophilic and lipophilic properties) [27,57,75]. There is little information on conversion efficiencies and production compositions of microemulsified bio-oils in literature.

2.3.4. *Alternative processes*

Shonnard et al. introduced the "UOP/Eni Ecofining" process, based on conventional hydro-processing for converting bio-oils to branched paraffin rich diesel fuel [9]. Hydro-deoxygenation, decarboxylation and hydro-isomerization reactions occur. As outlined in Fig. 6, the process was carried out in a catalytic reactor with hydrogen gas (H_2) at unspecified reaction temperatures. The deoxygenated liquid product is then separated from water, CO_2 and H_2 and fractionated to remove light products.

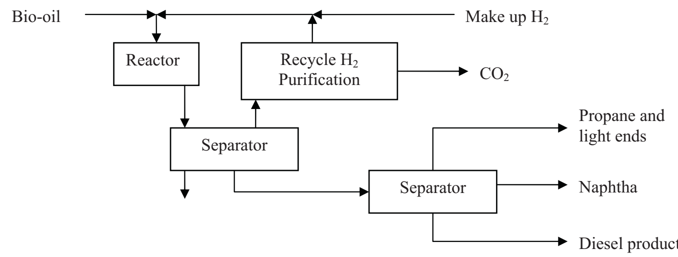


Fig. 6. "UOP/Eni Ecofining" process [9].

Vegetable oils such as palm, rapeseed, jatropha and soybeans were tested and through varying H_2 concentrations a feed conversion of 100% was achieved [9]. Bio-oils with high SFA as found in recycled oils (tallow oil, fish oil and waste greases) would potentially consume less hydrogen in the process, but would require pretreatment for salts and solids. Use of existing refineries and fuel distribution systems are possible with the process. The main product is an aromatic sulphur free substance ("green diesel"), which can vary between 88 and 99% (v/v) of total product, with propane and naphtha as co-products. The main product was similar to petroleum diesel in terms of carbon number range and molecular weight however, the aliphatic part was only partially saturated.

As an option to transesterification, ozone treatment was investigated by Murakami et al. for producing biodiesel from waste fish oil [76]. The process as outlined in Fig. 7 involves pretreatment where the bio-oil is filtered using kaolin, reacting with ozone in the presence of a catalyst (primary ozone treatment), followed by filtering with zeolite, and reacting again with ozone (secondary ozone treatment). In this process, ozone, due to its low oxidation stability decomposes to produce active oxygen, which decomposes the bio-oil. A catalyst was added (calcium phosphate monobasic or iron oxide) to prevent polymerization of the oil during primary treatment. The process was tested for waste fish oil, and properties of the resulting product are discussed in Section 3.4.4. Conversions for primary and secondary ozone treatment of fish oil were 96% and 95%, respectively. The low boiling point fractions of fish oil increased with ozone treatment, where mainly hydrocarbons were present in the product and undecane was the predominant alkane [76].

Dilution of crude bio-oils with diesel fuels, solvents or ethanol is another method of improving bio-oil properties [10]. Bio-distillation, using existing petroleum processing refineries with minimal modifications, is a method under research in North America [2].

2.4. Bio-oil (biodiesel) standards

Standards have primarily, but not exclusively, focused on biodiesel. Austria was the first to prepare and approve biodiesel standards and was for rapeseed oil methyl ester [44]. Biodiesel standards have two components; general fuel based parameters similar to those of diesel fuels, and chemical composition and purity based parameters for fatty acid alkyl esters. The latter is used to address biodiesel from different origins. Fuel based parameters are given in Table 6, and Table 7 summarizes the quality based parameters.

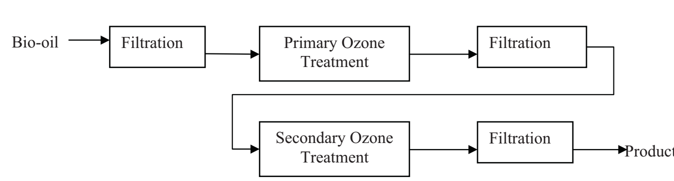


Fig. 7. Ozone treatment of bio-oils [76].

Table 6
Fuel based parameters of biodiesel [44].

Parameters	Unit	Austria (ON[a])	Czech Republic (CSN[b])	France (Journal Officel)	Germany (DIN[c])	Italy (UNI[d])	USA (ASTM)
Density at 15 °C	kg/m^3	850–890	870–890	870–890	875–890	860–900	–
Viscosity at 40 °C	mm^2/s	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	1.9–6.0
Flash point	°C	100	110	100	110	100	130
CFPP	°C	0/−5	−5	–	0–10/−20	–	–
Pour point	°C	–	–	−10	–	0/−5	–
Cetane number		≥49	≥48	≥49	≥49	–	≥47
Neutralization number	mg KOH/g	≤0.8	≤0.5	≤0.5	≤0.5	≤0.5	≤0.8
Conradson carbon residue	wt.%	0.05	0.05	–	0.05	–	0.05

[a] Österreichisches Normungsinstitut.
[b] Czech Standards Institute.
[c] DIN Deutsches Institut für Normung.
[d] Ente Nazionale Italiano di Unificazione.

Table 7
Quality based parameters of biodiesel [44].

Parameters (mass %)	Austria (ON)	Czech Republic (CSN)	France	Germany (DIN)	Italy (UNI)	USA (ASTM)
Methanol/ethanol	≤0.2	–	≤0.1	≤0.3	≤0.2	–
Ester content	–	–	≥96.5	–	≥98	–
Monoglyceride	–	–	≤0.8	≤0.8	≤0.8	–
Diglyceride	–	–	≤0.2	≤0.4	≤0.2	–
Triglyceride	–	–	≤0.2	≤0.4	≤0.1	–
Free glycerol	≤0.02	≤0.02	≤0.02	≤0.02	≤0.05	≤0.02
Total glycerol	≤0.24	≤0.24	≤0.25	≤0.25	–	≤0.24
Iodine number	≤120	–	≤115	≤115	–	–

Iodine value (IV) is a measure of oxidation stability of a bio-oil and is based on total unsaturated fatty acids (MUFA and PUFA) and correlates with cetane number and viscosity [45]. Iodine value is not incorporated into ASTM standards and is associated with the European Union (EU). The use of IV as an indicator for oxidation stability is debated, as although higher IV values indicate lower stability, the reverse is not a given. For example, oils with a high level of unsaturated FA would have high IV and therefore would indicate low stability; however, the type of unsaturated FA (PUFA vs. MUFA) also impacts the stability in that high PUFA levels lower stability to a greater extent than MUFA.

2.5. Engine performance of refined bio-oils

2.5.1. Biodiesel

A comparison of properties of biodiesel produced from waste and virgin oils is given in Table 8. Conversion of crude bio-oils to their ester form improves lubricity and reduces premature wearing of fuel pumps [77]. Biodiesel has low volatility and high viscosity, therefore at low temperatures it may gel and cause engine filter clogging and problems in pumping to and from engines [15,77]. Blending with No. 2 diesel can improve fuel properties by decreasing pour point cloud points, and IV. In addition, blending improved the lubricity of ultra low sulphur petroleum diesel fuels [12,78]. The most common blend is B20 [10].

The use of biodiesel in engines generally results in increases in nitrous oxide (N_2O) emissions, and possible crystallization below 0 °C resulting in separation of diesel from blend and plugging of fuel lines and filters [10]. These can be improved through branched chain esters such as isopropyl esters and/or winterization or inducing crystallization through cooling [79,80]. Winterization allows the residual solids to be filtered after the solution reaches equilibrium with the esters at a cloud point below and pour point above the typical values. Saturated fats can be removed through winterization, leaving oil with higher long chain fatty acids [81]. Additives can also improve the pour point without impacting the cloud point [80].

2.5.2. Oil from pyrolysis

Compared to their crude oil feedstock, pyrolyzed products have low viscosities and high cetane numbers [10]. The sulphur, water, sediment content, and copper strip corrosion values were within acceptable range for pyrolyzed vegetable oils; however, drawbacks include high ash content, carbon residue, and pour point compared to diesel fuels. Waste fish oil was treated with fast pyrolysis followed by distillation and the resulting bio-oil boiling range was similar to gasoline and diesel [74]. The use of pyrolyzed bio-oils in engines has resulted in carbon deposits and lubricating oil contamination [17]. Engine tests were mostly limited to short term durability tests [10].

Table 8
Properties of biodiesel produced from several feedstocks [8,19].

Property	Mahua biodiesel	Methyl soyate	Ethyl tallowate	Ethyl greasate	Diesel
Density at 15 °C (kg/m^3)	880	–	–	–	850
Viscosity at 40 °C (mm^2/s)	3.98	4.3	5.2	6.2	2.60
Flash point (°C)	208	–	–	–	68
Pour point (°C)	6	−2	3	−1	−20
Water content (wt.%)	0.04	–	–	–	0.02
Ash content (wt.%)	0.01	–	–	–	0.02
Carbon residue (wt.%)	0.2	–	–	–	0.17
Acid value (mg KOH/g)	0.41	–	–	–	0.35
Calorific value (MJ/kg)	37	39.8	39.6	39.9	42
Stability	–	–	–	–	Good
Cloud point (°C)	–	0	15	5	–

Table 9
Results for short term testing of microemulsified vegetable oils in engines [82–85].

Type of feedstock	Microemulsion	Solvents	Carbon deposits	Engine performance	References
Crude soybean oil	Ionic and non ionic	Aqueous ethanol		- Low cetane no. and energy content than No. 2 diesel	[82]
Alkali refined and winterized sunflower oil	Non ionic	53.3:13.3:33.4 (v/v, %) of oil:ethanol:1-butanol	Heavy carbon deposits	- No deteriorations in performance - Irregular injector needle sticking - Incomplete combustion - Increase in lubricating oil viscosity	[83]
Degummed and alkali-refined soybean oil	Non ionic	50:25:5:20 (wt.%) of No. 2 diesel:oil:ethanol:1-butanol	Deposits in in-take valves, tops of cylinder liners, injector tips	- Passed the 200 h engine performance tests and performed better than sunflower oil blends with diesel	[84]
Soybean oil	(Not given)	52.7:13.3:33.3:1 of oil:methanol:2-octanol:cetane improver		- Carbon deposits in injector nozzles and exhaust valves	[85]

2.5.3. Microemulsified oils

Microemulsion produces oils with higher latent heat of vapourization, lower viscosity, improved spray characteristics, and better ability to cool down engine chambers reducing coking, than diesel fuels; however, with lower volumetric and heating values compared to diesel fuels [10,17]. Studies comparing microemulsified bio-oils and conventional petroleum fuels are outlined in Table 9. Deposits in injector nozzle orifices and exhaust values in engines even in short term use, have limited use of microemulsified bio-oils [10].

2.6. Emission comparison for bio-oils

Most studies on emissions have focused on biodiesel. Neat biodiesel (B100) has shown emission reductions of 73% CO_2 (on a life cycle basis), 67% unburnt HC, 48% CO, 47% PM, 100% SO_2 and 80% polycyclic aromatic hydrocarbon (PAH) emissions, when compared with diesel [7]. However, in this same reference there is 10% increase in NO_x emissions. Lower CO_2 emissions are attributed to the additional oxygen in the biodiesel. The study by USEPA performed a life cycle analysis on engine exhaust emissions using 20% blends with diesel and 100% of soybean oil, rapeseed oil, and animal fat based biodiesels. Particulate emissions and CO were reduced, while NO_x emissions increased slightly in all three cases [86]. The highest overall PM and CO reduction and lowest NO_x increase occurred in the 100% animal fat based biodiesel, which was a combined feedstock of tallow, grease and lard. Shonnard et al. used soybean based "green diesel" and reported 83.6–85.2% GHG reduction over the life cycle from raw material extraction, production through to engine use, compared to petroleum diesel fuels [9]. This value was slightly lower than soybean biodiesel.

Biodiesel derived from virgin oils also had higher net energy benefit compared to most petroleum fuels [7]. For example, 0.83 units of energy are returned per unit of energy consumed for petroleum diesel, while for vegetable oil based biodiesel the value is 3.2.

Waste oil based biofuels derived from animal fats had lower life cycle based gaseous emissions than virgin vegetable oils when the crops are harvested or produced specifically for biodiesel production [7]. Natural Resources Canada conducted an LCA study on GHG emissions of biodiesel produced from canola oil, soy oil and animal fats (a combined feedstock of yellow grease and tallow) in use as a transportation fuel [87]. Table 10 outlines percentage reductions in emissions for blend of B20 and neat biodiesel (B100), compared with petroleum diesel fuels, modified from NRC (2002) data as given in Boyd et al. [7]. Animal fat based neat biodiesel show the highest reduction in CO_2, CH_4, CO, chlorofluorocarbon (CFC) + hydrofluorocarbon (HFC), sulphur dioxides (SO_x) and PM emissions, and the lowest increase in NO_x emissions.

The sustainability of communities may also be positively impacted by biofuel use through possible in-community biofuel production/processing, use of local materials/wastes, and use in the community itself [7]. This would result in reduction of dependency on transportation costs associated with fuel, lower the instability associated with petroleum fuel price fluctuations, creation of new expertise, economic development, and overall reduction in GHG emissions and other human and environmental impacts.

3. Biofuels from fish processing plant waste

3.1. Fish waste: characteristics, composition and current by-product recovery practices

3.1.1. Generation and characteristics

Waste generated from fish processing plants is approximately 50 wt.% of harvested fish depending on the type of fish, product

Table 10
Percentage reductions in emissions by substitution of petroleum fuels with several biodiesel products.

	B100 biodiesel			B20 biodiesel		
	Canola	Soy	Animal fat	Canola	Soy	Animal fat
GHG						
CO_2	−67%	−67%	−73%	−13%	−13%	−14.2%
CH_4	−39%	−40%	−51%	−8%	−8%	−10%
N_2O	+99%[b]	+162%[b]	−1635%	+19%[b]	+31%[b]	−3%
Total CO_2 equiv	−64%	−63%	−92%	−12%	−12%	−18%
Non-GHG						
CFC + HFC	0%	0%	0%	0%	0%	0%
CO	−70%	−69%	−74%	−13%	−13%	−14%
NO_x	+53%[b]	+52%[b]	+2.7%[b]	+10%[b]	+10%[b]	+0.5%[b]
VOC[a] ozone weighted	−43%	−42%	−28%	−8%	−8%	−5%
SO_x	−20%	−21%	−43%	−5%	−5%	−9%
PM	−12%	−12%	−39%	−4%	−4%	−9%

Modified from [7,87].
[a] Volatile organic carbons.
[b] Percentage increments.

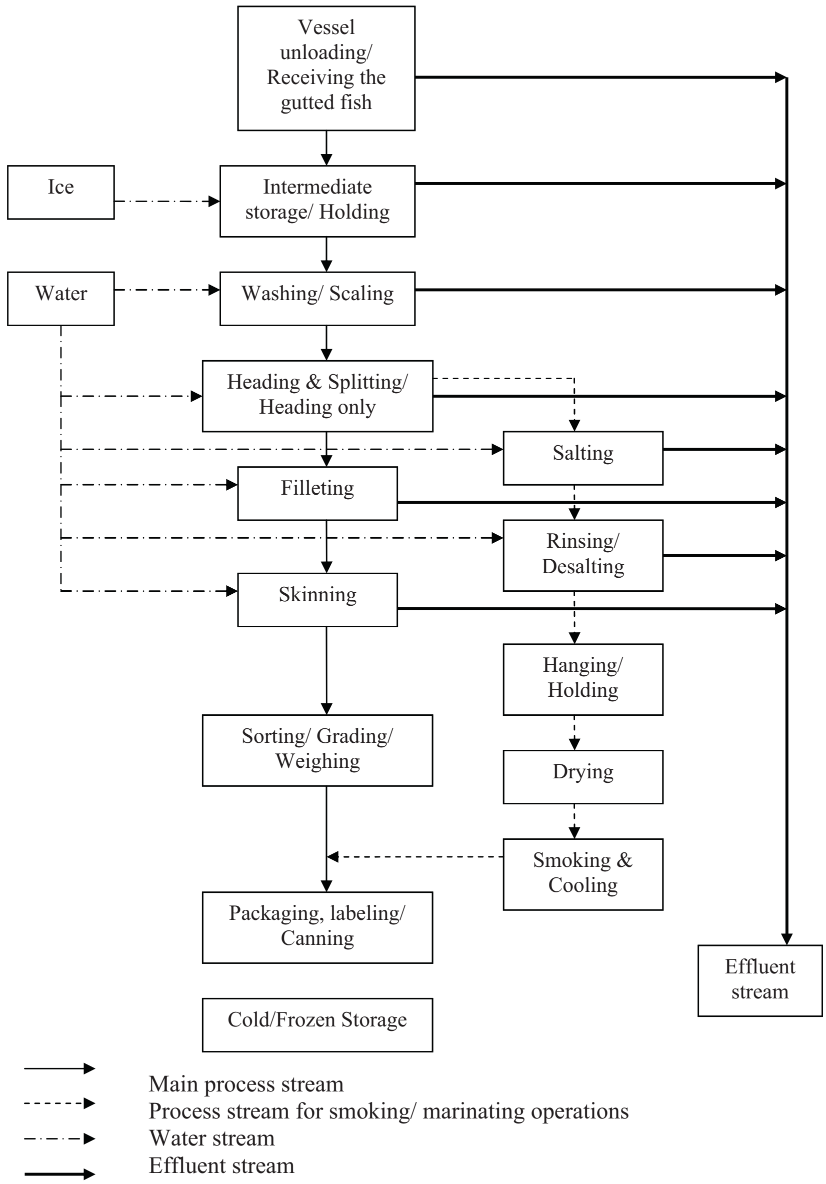


Fig. 8. Process flow for ground fish and herring processing in Atlantic Canada [89].

and processing techniques [34,88]. For example, as a percentage of total landed weight, 40% of prawns, 39% of crustaceans, 14% of mussel, 32% of crabs, 35% of brown shrimp and 35–45% of catfish are produced for human consumption. The processing varies considerably, however a "general" process used mainly in ground fish, herring and salmon processing plants in Atlantic Canada is outlined in Fig. 8. Shell fish processing has different features to the flow given in Fig. 8, as lobster and shrimp processing involve butchering or cooking of live catch [89].

The resulting effluent is from pump water from fish unloading operations, washed water from fish cutting operations (filleting, skinning, heading, peeling, butchering of live fish), and brine water from curing [89]. Vessel unloading is carried out using wet pumps to allow smooth handling of fish, during which part of the circulating water is separated through gratings and discharged to the wastewater stream. Residual water from large wash tanks used for washing of fish prior to cutting may also enter the wastewater. Cutting operations use a continuous water flow to allow for removal of impurities. Fish parts such as skin, bones, liver, viscera, belly trimmings, gut material and kidney mixed with blood water are discharged with the effluent. Specific to salmanoid and pelagic fish discards are down-graded whole fish parts, filleting by-products such as heads, belly flap trimmings and frame bones. In addition, preservatives such as phosphate, chlorine from sanitation water, chlorides, disinfectants, dockside waste, sulphates, polychlorinated biphenyl (PCB), brine water and fecal coliform from seabirds attracted to the waste also end up in the effluent stream [89–91].

Several papers have characterized the effluent in terms of solid content, BOD, chemical oxygen demand (COD), and FOG [89,92,93]. Solids were analyzed for total, suspended, volatile and dissolved solids. Table 11 summarizes results from plants from Canada, the USA, and Egypt. Constituents of the waste varies with fish type, season and the processing systems, however high BOD, total suspended solids (TSS), up to 60% FOG from butchering processes and high nitrogen content due to high blood and slime were common to all wastewaters [89–91]. Fishmeal plants generate wastewater with higher organic substances and solids than the upstream processing plants.

The effluent also can be odourous and has high turbidity [57]. The pH varies depending on the type of plant and is typically slightly acidic [92,94–97]. Fishmeal plant's effluent pH values

Table 11
Fish waste characteristics from studies in Egypt, USA and Canada [89,92,93].

Fish/plant type	COD (mg/L)	BOD (mg/L)	TSS[a] (mg/L)	TS[b] (mg/L)	TDS[c] (mg/L)	FOG[d] (mg/L)
Tuna (NC[e])	1600	700	500	–	–	250
Tuna (all Canada)	–	895	1091	17,900	–	–
Bottom and fin fish (NC)	400–2000	200–1000	100–800	–	–	40–300
Fishmeal stick water (NS[f])	140,000	48,000	20,000	–	–	–
Fishmeal (NC)	150–42,000	100–24,000	70–20,000	–	–	20–5000
Fishmeal (NB[g])	1170–89,800	30–6470	18,530–50,100	18,530–50,100	–	–
Breaded shrimp	1200	720	800	–	–	–
West coast shrimp	3300	2000	900	–		700
Sardine and mackerel (Egypt)	1222–1431	870–1167	3745–5071	–	6217–7861	215–400
Sardine packing (all Canada)	–	100–2200	100–2100	–	–	–
Shell fish (NB)	720–13,440	470–4640	180–5260	1080–22,300	–	–
Ground fish (NB)	496–9450	180–4000	210–438	14,240–40,000	–	–
Ground fish (dry, all Canada)	–	45–990	14.4–908	–	–	–
Ground fish (wet, all Canada)	–	146–1205	30–1550	–	–	–
All herring	3000–10,000	1200–6000	600–5000	–	–	600–800
Herring (cleaning water, NB)	960–4800	360–2440	270–2150	264–1947	–	–
Herring (pickle water, NB)	64,000	17,920	5833	2300	–	–
Herring (NB)	–	440	500	–	–	–
Crab, lobster, mackerel, herring (NB)	–	330	100	–	–	–
All salmon (NC)	300–5500	253–2600	120–1400	–	–	20–550
Salmon (all Canada)	–	1.54–29.1	0.26–22.6	–	–	–
Snow crab, herring (NB)	–	310	79	–	–	–
Shrimp, crab, herring (NB)	–	1700	1195	–	–	–

[a] Total suspended solids.
[b] Total solids.
[c] Total dissolved solids.
[d] Fats, oil and grease.
[e] North Carolina.
[f] Nova Scotia.
[g] New Brunswick.

varied between 6.3 and 6.9 range [95,97]. Effluent from fish canneries processing tuna and mussel in Spain had a pH value of 8.10, although the cooking process effluent was between 6.18 and 6.95 [94,96]. For shell fish such as blue crab, soft shell clams and Atlantic oyster effluents, pH values were 7.63, 7.11 and 7.15 respectively [92].

3.1.2. Chemical composition

The chemical composition of the effluent depends on the harvesting region, season, type of fish, and type and extent of processing. Lipids, proteins, metals, carbohydrates and moisture are the main constituents of the discarded fish parts. Among these, lipids, volatile solids, ash and protein are important factors in determining the end use of the recovered oil as fuel. Ash content is used for estimating inorganic components or metals and several papers have estimated the percentage proximate composition [88,94,98–100]. Average composition of fish by-products is given in Table 12. High moisture and protein were common to all species processed [31,89]. Ash content is generally lower than 4 wt.% for most fish waste, and lipid content varies depending on the type and part of the fish [32,57,98,99].

Based on the lipid content, fish are categorized into four groups; lean fish containing 2% fat (e.g. cod, haddock and pollock), low fat containing 2–4% fat (e.g. sole, halibut and red fish), medium fat containing 4–8% fat (e.g. most wild salmon), and high fat containing 8–20% fat (e.g. herring, mackerel and farmed salmon) [101,102]. Cod, haddock, hake, skate, ray and sharks mostly contain liver oil, while mackerel, herring and pilchard contain muscle oil [34]. In pollock, the major percentage of lipids (between 30 and 40%) is found in the liver [21]. Salmon have higher fat content in the viscera than the fillet [101]. Within the same type of fish the composition can vary depending on the type of tissue (light or dark muscle) [103]. For example, salmon light muscle had 20.4% protein and 2.1% fats and oils, whereas the salmon dark muscle contained 17.5% protein and 12.5% fats and oils. Marine species with red flesh generally contain higher lipid content than white flesh ones.

Metals such as arsenic, lead (Pb), mercury (Hg), and cadmium (Cd) were detected at low concentrations in waste from trout plants [98]. Phosphorous and magnesium (Mg) were 1.08 and 1.25 wt.% on a dry basis, for pink salmon livers [99]. Zinc (Zn), Mg, calcium (Ca), iron, manganese, Cd, Pb and nickel were detected below 1 wt.% for liver discards of salmon, walleye pollock and pacific halibut. High salinity in fish processing wastewater is attributed to ions in the fish and water use and cooking during processing [94]. Tuna and mussel cooking effluents had chloride values ranging from 11.39 to 13.66 g/L [94,96]. Average concentrations for sardine and mackerel fish canning facility effluents from Egypt were 500–697 mg/L sodium ions, 60–70 mg/L potassium ions, 4.7–6.2 mg/L ammonium, 0.15–0.55 mg/L sulphate, and 13–17 mg/L phosphate [93].

3.1.3. Current practices in by-product recovery

Recovery of by-products from fish processing effluent occurs at some plants, however this is not the case in majority of remote communities (e.g. Atlantic Canada sends solids to landfills and wastewaters are typically discharged to the marine environment) [89]. When waste effluent is utilized it is done to produce fishmeal/oil, silage (product from fermentation of fish waste), and organic fertilizer [98].

Fishmeal plants are of particular interest as the major by-product of this process is waste oil [98]. Some regions (e.g. EU) have imposed a ban on feeding of fishmeal to ruminants [34]. The residual fish oil is used for a variety of purposes depending on the quality, such as for metal processing, leather treatment and production of margarine, peanut butter, ink, soap, rubber, lubricants, paints, varnishes, fire retardants, fungicidal derivatives, rust inhibitors, candles, water repellents and plasticizers. Globally (in 2002) 56% of fish oil was used for aqua feed, 30% for edible oils, 12% for industrial purposes, and 2% in the pharmaceutical industry [7]. The use and processing of crude fish oil as a fuel has some history and will be discussed in subsequent sections. Fishmeal plants are not widespread, especially at remote fish processing plants due to high costs of operation, low waste volumes associated with the fish

Table 12
Average chemical composition of fish waste (wt.%) [32,57,88,94,99,101].

Type of fish	Fish part	Protein (wt.%)	Moisture (wt.%)	Ash (wt.%)	Lipid/oil (wt.%)	Reference
Pink salmon	Liver (6–16% of fish)	18.61	76.6	1.5	3.3	[99]
Walleye pollock	Liver (9–32% of fish)	7.77	41.04	0.89	50.3	
Pacific halibut	Liver	13.36	73.31	1.3	12.04	
Pacific cod	Hand filleting	15.0	79.2	4.1	4.1	[57]
	Machine filleting	14.1	79.4	3.8	3.8	
Pollock	Hand filleting	11.3	81.3	3.6	3.6	
	Machine filleting	12.5	82.0	3.7	3.7	
Salmon	Head	14.2	71.4	3.9	3.9	
	Viscera	17.1	78.3	1.8	1.8	
Sardine and mackerel		699–910 mg/L (in effluent)	–	–	–	[94]
Cod	Viscera	22.1	–	1.8	74.4	[32]
Salmon	Viscera		59.4	–	24.1	[101]
Catfish	Whole viscera (33.6% of fish)	14.7	50.1	–	33.6	[88]
	Digestive tract	13.4	79.5	–	5.8	
	Liver	11.4	74.9	–	8.8	
	Gold bladder	2.6	88.9	–	0.3	
	Visceral storage (10% of fish)	1.3	8	–	90.7	
	Fillet	14.4	74.4	–	9	
	Nugget	13.5	71.2	–	14.7	

plant itself, low value of fish waste, high cost of transportation to a central fishmeal facility (to overcome volume issues), and odour issues [104].

Other possible by-products from fish/shellfish waste include chitan and chitosan for food preservatives, fish protein hydrolysate, fish protein concentrate, carotenoid pigment, minerals, flavours, enzymes, leather, glue, pharmaceuticals, gelatine, cosmetics, fine chemicals, collagen, pearl essence, antioxidants, and food additives [34,98].

Separation of the "oil" from the fish waste can prove challenging as processors need to balance oil recovery with technical/operation ease and costs.

3.2. Oil recovery processes and parameters

Physical, thermal, and biological processes, and chemical extraction using solvents have been used at industrial and lab scale to recover oil from fish plant discards [6,105]. Physical and thermal separation is used in the fishmeal industry to separate oil from the meal. Biological processes include fermentation or ensilaging and enzymatic hydrolysis [6]. In enzymatic hydrolysis, the focus is recovery of proteins from the waste and oil is recovered as a by-product. Solvent extraction is used for fat/lipid extraction at the lab scale; however this may be limited in the fish processing industry due to high energy costs, requirement to build new facilities,

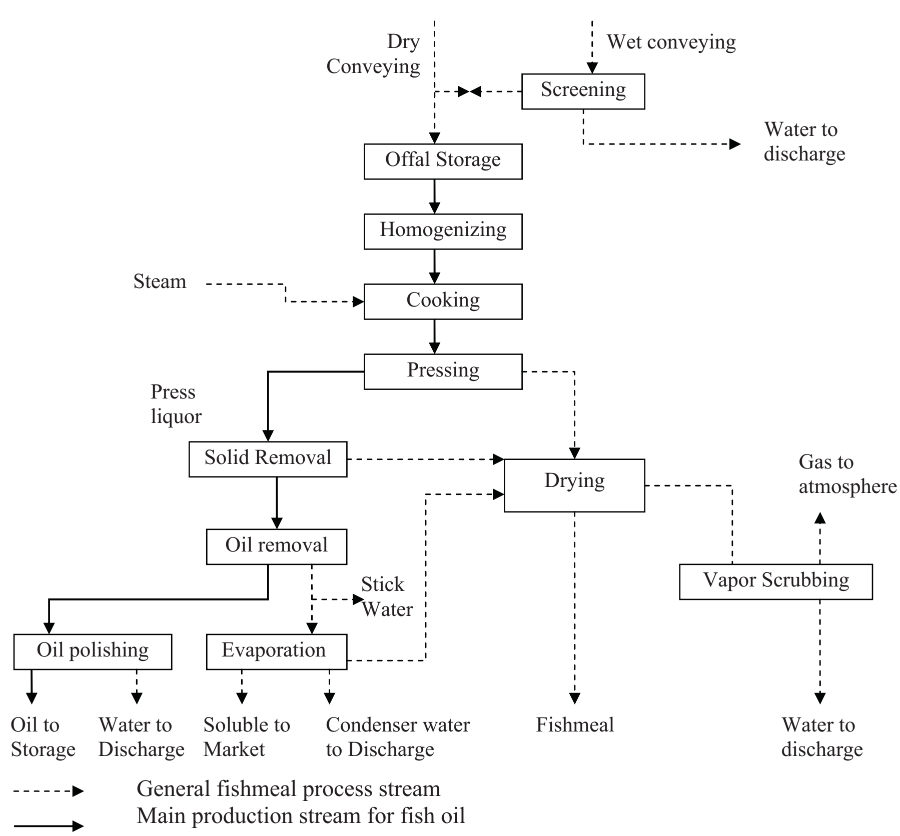


Fig. 9. General process flow in fishmeal plants [89,106].

and additional wastewater treatment requirements. The various processes are outlined in Section 3.2.1.

3.2.1. Physical/thermal separation processes

3.2.1.1. Fishmeal process for producing oil. The process flow for fishmeal/oil production used in fishmeal plants is outlined in Fig. 9. Effluent from processing plants is first sent for storage in pits or tanks until sufficient volumes are collected to process to fishmeal [89,106]. The fish oil is recovered from the fishmeal plant waste by homogenizing the waste, heating or cooking to release the oil, removal of solids by pressing, separation of oil from residual solids and water, and oil polishing [89,106].

In the homogenizing step, hashers are used for breaking the fish into smaller parts prior to processing [106]. At lab scale homogenizing is carried out through mincers, grinders or blenders [23,24,101]. In heating also known as "cooking", fat cells rupture and liberate the oil [106]. Heating also coagulates the protein and frees the chemically bound water. Traditionally, heating temperatures range from 95 °C to 100 °C for a period of 15–20 min. Although fat cells start to crack at temperatures less than 50 °C, the moisture content does not reach the optimum 10–12% until 65–120 °C [98]. Fishmeal plants operate at high cooking temperatures to ensure uniform temperature in heating material. Although heating conditions can depend on the type of fish, size, oil content and condition, heating at high temperatures for long durations may not be necessary [16,106]. Over-cooking can result in formation of large suspended solids which reduce pressability [106]. Sathivel et al. added water at a ratio of 5:1 (water:ground viscera) followed by heating at 70 °C for 15 min and obtained better separation of the visceral oil [24].

Direct and indirect heating cookers are used in the fishmeal industry [106]. Indirect steam cookers are equipped with a surrounding steam heated jacket, steam heated rotor, and a rotary screw conveyer. Live steam is added to the raw material to increase the efficiency of the process. Contherm cooking is a new technology that rapidly heats the material within 2 min and provides effective temperature control, easier dismantling, and cleaning. By adding stick water the heat transfer rate is improved and there is a reduction in viscosity of raw material. Some plants use pre-cookers to reduce the load and prevent scaling in main cookers. Direct steaming and vacuum cooking are also used as heating methods for extraction of liver oil [34].

Pressing is carried out to squeeze liquid from the slurry and to increase the yield of meal. Heating during pressing removes much of the moisture from the press cake, and at higher temperatures the oil viscosity is reduced but at the expense of protein denaturation and reduced oil release. Screw presses are sometimes used in conjunction with chemicals such as formaldehyde or calcium chloride ($CaCl_2$); however this reduces the nutritional quality of the oil and increases the residual chloride in the meal. The solids and liquids can also be separated using decanters (centrifuge) that can replace the press [23,106]. The advantages of using centrifuges are process simplicity, better process control, reductions in heat load on the material due to faster process, ability to process soft and very fluid like material, and better washing. Disadvantages are products having comparably higher moisture content, and formation of emulsions and fine particles making separation of oil difficult [106].

The press liquor has oil, water, sludge and solids in both suspended and dissolved forms [106]. On average 70% of the raw material ends up as press liquor while the rest is press cake. The liquor is sent to settling tanks where sludge collects at the bottom, oil on top, and the water layer in the middle. Centrifuges are used to enhance the efficiency in settling where the liquor is preheated to 90–95 °C prior to centrifuging. Suspended solids are removed using decanter centrifuges or desludgers. The processing capacity of available decanters is 12–300 t/d, therefore smaller plants use vibrating strainers to achieve the same result.

Vertical disc centrifuges of the nozzle type or self cleaning centrifuges are used for separation of stick water from the oil [106]. Miyashita et al. used a desludger at lab scale to separate the oil from liquid, where simultaneous separation of the sludge, water and oily phase was carried out using two consecutive three phase centrifuges (operating at $7370 \times g$ and $9940 \times g$) [16]. The oil phase is dewatered using a high speed centrifuge (operating at $15{,}500 \times g$), at temperatures of 10–17 °C. Sathivel et al. used filtration, pressing using a cheese cloth followed by centrifugation at 500 rpm for 30 min for separating crude fish oil from water and residual removal [24].

The final step in preparation of oil is polishing, which serves to extract impurities and facilitates oil stability during storage [106]. Hot water is mixed with the oil feeds at 95 °C and the oil/water mix is typically centrifuged at 5000 rpm.

In general, oil is recovered both at commercial and lab scale using a typical fishmeal process, with minor modifications in heating and oil separation conditions.

3.2.1.2. Other process: lab and commercial scale. Rendering involves the addition of large amounts of water and steam hydrolysis of the fat cells until the fish waste is partially liquefied, and the oil is recovered through skimming or centrifugation [7]. In a study by Miyashita et al., sardine oil was separated from surimi produced effluent sludge using two consecutive three-phase centrifuges operating at high speeds [16]. Further separation of TAG was carried out by passing the oil through a column packed with n-hexane and diethyl ether at a ratio of 9:1. The oil recovered through this process can be used commercially for food grade applications without further refining.

3.2.2. Extraction using chemicals

Solvent extraction and acid based digestion are the two most common methods to separate oil at lab scale. These processes are focused on separating the lipid fraction with minimum impurities for analysis by chromatography for fatty acids and lipid classes. In these experiments various mixtures including methylene chloride, chloroform/methanol (2:1), chloroform/methanol/chloroform and methanol 2:1 mix/chloroform extracted water (2:1:1:0.5) were used for extracting oil from wastewater or fish bodies [14,16,23]. In acid digestion experiments carried out by Sun et al., concentrated HCl was used with tertiary butylhydroquinone (TBHQ) as an anti-oxidant for extracting lipids for fatty acid analysis [101].

3.2.3. Biological processes: enzymatic hydrolysis and fermentation

3.2.3.1. Hydrolysis. Enzymatic hydrolysis is used for recovering proteins from effluents in the fish processing industry where fish oil is a by-product [32]. In autolytic hydrolysis enzymes present in the fish itself are used, as fish viscera are rich in lipases [6,33,107–109]. However, this dependency on digestive enzymes and long reactor residence times has reduced the quality of the hydrolysates (compounds produced by hydrolysis) [32,109]. Raw materials with high lipid content can form protein–lipid emulsions during autolytic hydrolysis and reduce the oil yield [32,110,111]. In accelerated hydrolysis enzymes are added and temperature controlled to enhance product quality.

In experiments by Ivar et al., the effect of heating/temperature, initial water addition, and addition of two types of enzymes (lecitase and alcalase) on the product quality of cod by-products was investigated [32]. Initial heating increased the percentage oil recovered up to a high value of 51% and lowered protein-emulsion formation. However, the TAG production was reduced and impurity levels (e.g. PL, polar lipids) increased. It has been found that using lecitase as the enzyme reduces lipid degradation during hydrolysis [32,112]. The highest oil production and lowest emulsion

formation were achieved with alcalase enzyme without the addition of water.

Supercritical and sub-critical water hydrolysis has been investigated for recovery of oil from fish waste [103,113]. According to Yoshida et al., the subcritical process showed higher oil recovery from fish waste than the supercritical process and recovery of other useful organic materials such as pyroglutamic acid and amino acids (cysteine, glycine and alanine) occurred [113]. The subcritical water hydrolyzed product compounds were separated using an ion-exchange column [103].

3.2.3.2. Fermentation. Fermentation of fish waste is carried out by using bacteria and sugar or organic acids (e.g. lactic acid) producing silage and the oil is typically separated by centrifugation [6]. Acids generated in situ from microorganisms such as lactic acid bacteria have also been used in fermentation of fish viscera where the bacteria both oxidized and preserved the fat [6,114–116]. Silage preparation from fish viscera through bacterial addition in a study by Rai et al. resulted in a reduction in pH of fresh viscera from 6.1 to 4.5 after three days of fermentation. The higher acid value is attributed to bacterial lipases and delay in the fermentation process [6]. Significant differences in oil product were not observed between fermenting under natural conditions and controlled conditions. Advantages of fermentation/hydrolysis over physical separation methods include possible energy savings and recovery of other useful products such as protein hydrolysate and collagen.

3.2.4. Purification

Washing is typically required if the crude fish oil is used as an animal or fish feed [34]. Other methods such as solvent extraction are used; for example, Miyashita et al. used a slurry mixture of n-hexane, activated carbon, and celite 545 to remove tocopherols and pigments [16]. In this case the oil was further refined on a silicic (silica gel 60) acid column by washing with n-hexane and a mixture of n-hexane/diethyl ether solution (95:5, 90:10 and 80:20, v/v). A generalized chemical refining process flow for impurity removal is outlined in Fig. 3 and is used to remove FFA, odour, waxes and water from fish oil [24,34].

3.2.5. Preservation of feedstock and the recovered oil

The presence of high levels of protein, fats and enzymes in fish waste can cause enzymatic hydrolysis and microbial degradation resulting in reducing the quality of the recoverable oil [31]. High moisture levels also contribute to hydrolysis. Enzymes such as lipases in the gut material of high fat species such as salmanoids and pelagic result in the formation of FFA. The recovered oil can also be highly reactive and degrade easily, due to high levels of unsaturation and PUFA in fish oils. Oxidation of unsaturated fatty acids present in fish waste lipids results in bad odours [6]. For all of the above reasons preservation of the waste and recovered oil is essential.

Stabilization or preservation of the waste is achieved through chilling or icing, freezing, ensilaging with acids and freezing in combination with addition of antioxidants [31]. Use of ensilaging is not desirable, as the addition of formic acid results in lipid oxidation and hydrolysis. Ensilaging also increases FFA and volume of the waste, thereby increasing the cost of transportation and further processing. Chilling or icing is effective for short term storage, but increases the bulk of the material and the energy requirements. Chilling is advantageous since facilities are already available in the processing plants. Freezing can be costly due to requirement of space unless facilities are already present onsite. Salting needs further investigation in terms of biodiesel applications. Freezing in combination with addition of antioxidants is recommended as a preservation method for fish waste.

Storage in bulk tanks of the recovered oil results in moisture collection at the bottom and partial solidification of the oil during cold weather conditions causing difficulties in pumping [31]. Using mild steel tanks with water drainage facilities at the bottom, steam heated coils to prevent saturated oil from freezing during winter months, and good insulation mitigates these problems. Addition of synthetic anti-oxidants to crude or refined oils is another method to minimize lipid oxidation.

3.3. Chemical and physical properties of the oil and analysis methods

3.3.1. Lipid composition

Marine oils contain TAG of fatty acids with carbon atoms varying between 14 and 22 with multiple double bonds possible. Other lipids such as FFA, waxes, ethers, HC, PL, KET, and alcohols can also be present [24,31]. Lipid analysis is carried out through extraction with solvents such as chloroform and methanol and additional solvent development followed by thin layer chromatography (TLC) equipped with FID [14]. Hexane, diethyl ether, formic acid, acetone, methanol, chloroform solvent development systems are used [14,32]. Lipid composition of fish processing waste extracted using several methods is summarized in Table 13. Analysis of ozone treated fish oil by Murakami et al. contained aldehydes, KET and ramify chain alkanes in small quantity [76]. The chain length of fatty acids in TAG of the feed (fish oil) reduced through ozone treatment, including diglycerides and formed hydrocarbons. The predominant hydrocarbons in the ozone treated product were alkanes with carbon number between 9 and 14.

3.3.2. Fatty acid composition

Fish oil contains long chain PUFA (n-3 or omega-3), the prominent ones being EPA and DHA making it an attractive edible oil [16,101]. Cold water marine fish contain a large amount of omega-3 fatty acids with Atlantic herring, Atlantic salmon, rainbow trout and sardines having the highest omega-3 fatty acids while the lowest is in catfish [99,117]. In addition, 50 different types of fatty acids can

Table 13
Lipid composition of oil recovered from fish waste [6,16,23,32,99,103].

Raw material	Lipid recovery method	Analysis method	TAG (wt.%)	FFA (wt.%)	Other (wt.%)	Total lipid recovery	Reference
Catfish Viscera	Solvent extraction	AOAC procedure 985.14	–	–	–	–	[23]
Walleye pollock	Solvent extraction	–	92.15%	3.28%	–	–	[99]
Pacific halibut	Solvent extraction	–	89.94%	1.87%	–	–	[99]
Sardine by-products	Solvent extraction	TLC/FID	>99%	–	–	–	[16]
Whole sardine	Solvent extraction	TLC/FID	85%	1%	13.5% PL	–	[16]
Fish by-products	Enzymatic hydrolysis	–	65–89%	0.2–1.2%	3% cholesterol, 7.6% PL and polar lipids	87–97%	[32]
Sardine by-products	Centrifugal separation	TLC/FID	>99%	–	–	–	[16]
Whole fish	Sub-critical water hydrolysis	–	–	–	–	0.2–64%	
Fish viscera	Fermentation	–	–	–	–	75–85%	

Table 14
Fatty acid composition of several fish discards [99,101].

	PUFA (mg/g)	MUFA (mg/g)	SFA (mg/g)	Total (mg/g)	Reference
Pink salmon livers	376.45	269.20	113.98	759.63	[99]
Walleye pollock livers	204.05	343.25	207.46	754.77	[99]
Pacific halibut livers	215.96	334.45	143.88	694.29	[99]
Farmed Atlantic salmon viscera	322.20	360.50	313.70		[101]

be present in fish oils [6,103]. To determine fatty acid composition a three step analysis is carried out; extraction of the fat, derivatization to their alkyl ester form and analysis [6,16,76]. The derivatized fatty acids are analyzed using GC/FID.

Godiganur et al. analyzed crude commercial fish oil by GC, the fatty acid profile was 24.8% stearic, 23.6% palmitic, 9.84% myristic and 6.56% octadecatetraenoic acids [118]. Bechtel et al. found fatty acids for Alaskan fish livers (pink salmon, walleye pollock and pacific halibut) were between C14:0 and C24:1. Seventeen types of fatty acids were detected for the farmed Atlantic salmon viscera in a study by Sun et al. [99,101]. Further analysis of the PUFA composition by Sun et al. showed 6.99% DHA and 7.91% EPA. In a study of salmon offal (viscera, whole fish, filleting by-products, heads, trimmings, skins and frame bones) by Skara et al., the omega-3 fatty acid (21.7% of offal) contained 9.9% EPA and 11.8% DHA [23]. A summary of fatty acid composition values for several fish by-products is given in Table 14. Catfish visceral parts showed high levels of unsaturated fatty acids in a study by Sathivel et al. [88]. The breakdown in this study showed unsaturated fatty acids of 307.6 mg/g for nuggets, 261.3 mg/g for whole viscera, 259.3 mg/g for visceral storage fat, 102.1 mg/g for digestive tract, 94.7 mg/g for gall bladder and 28 mg/g for liver of catfish.

Oil recovered from work involving fermentation or enzymatic hydrolysis of fish viscera had equal distribution of saturated and unsaturated fatty acids between C-14 and C-24 [6]. Palmitic, stearic, oleic, linoleic and linolenic acids were the major fatty acids in the oil and the predominant fatty acid and SFA were oleic acid and palmitic acid respectively. In the fresh viscera the distribution was 1.79% EPA and 2.84% DHA in fresh viscera while the fermented product had between 1.41–1.74% and 2.54–3.02% of EPA and DHA. The amount of unsaturated fatty acids remained constant during fermentation. A study involving surimi wastewater by Miyashita et al. showed EPA (15.9%), DHA (11.6%) and palmitic acid (15.9%) were the main fatty acids in the recovered oil [16]. Experiments using subcritical water hydrolysis of horse mackerel waste to recover oil carried out by Terashima et al. contained mainly EPA and DHA [103].

In the experiments using ozone to recover oil from waste by Murakami et al. the raw fish waste oil was analyzed using both GC/MS qualitatively, and GC/FID quantitatively [76]. Very small quantities of EPA, DHA were detected and the main fatty acids found were myristic, palmitic, stearic, oleic and linoleic. Fatty acid composition of biodiesel produced through transesterification of oil recovered from fish discards was analyzed by Lin et al., and was 20.94 wt.% oleic, 19.61 wt.% palmitic, 5.24 wt.% stearic and 15.91 wt.% DHA [119]. The percentage long chain fatty acids (C20–C22 range) and SFA were 37.30 wt.% and 37.06 wt.% respectively, while percentage PUFA in the fish biodiesel was 28.46 wt.% compared with 0.64 wt.% in waste cooking oil based biodiesel.

3.3.3. Thermal properties

Thermal properties of the waste and fish oil are critical for determining storage conditions, end uses and overall stability. A summary of thermal properties (melting point, enthalpy of melting and specific heats) from various studies for fish oils at different steps in the processing is given in Table 15. As the table indicates, the melting point decreased with each purification step and the deodourized oil showed the highest melting point reduction [24]. Removal of impurities at each purification step did not affect enthalpy of the melting range.

Thermogravimetric analyzer (TGA) uses the initial temperature and amount of weight losses during heating as indicators of thermal stability [21,121]. Weight loss is due to decomposition or interactions between compounds such as phospholipids, complex metals, minerals, FFA, peroxides and other oxidation products present in the oil. Stability is indicated by high initial temperature of decomposition. Analysis of crude pollock oil in the TGA in an air atmosphere by Sathivel et al. showed large weight loss at temperatures of 200–450 °C that increased with temperature, where complete decomposition occurred at 535 °C [21]. In an air atmosphere oxidation can occur due to absorption of oxygen and formation of peroxides which will present a gain in mass [21,121]. However, weight gains did not occur in pollock oil and the weight loss characteristics of red and pink salmon oils as studied by Sathivel were similar to pollock oil [21,120]. Thermal decomposition was higher in purified fish oils than crude fish oils due to higher availability of heat for evaporation of volatiles in purified oils and the reductions in heat absorption by impurities [21].

3.3.4. Rheological and cold temperature properties

Rheological properties are important parameters to determine how the fish oil/waste can be transported and handled [21]. Viscosity is a key indicator of flow characteristics and is measured using rheometers. The apparent viscosity of pollock oil as measured by Sathivel et al. at a shear rate of $500\,s^{-1}$ and at 20 °C was 0.04 ± 0.001 Pa s [21]. In the same study the flow behaviour index of pollock oil ranged from 0.8 to 0.9, exhibiting non-Newtonian behaviour and indicating that the viscosity can be reduced by increasing the shear rate.

Viscosity, cloud and pour point of fish oil ethyl esters were tested by Wilson's fuels of Nova Scotia in their pure form and with blends with No. 2 diesel fuel [77]. The ASTM D 2700-91 and

Table 15
Thermal properties of crude and purified fish oils [21,24,120].

Type of fish	Purification step	Melting range (°C)	Enthalpy (kJ/kg)	Specific heat capacity at 20 °C (kJ/kg °C)	Reference
Catfish	Crude	−46.2 to 21.2	74.1	1.69	[24]
Catfish	Degummed	−45.9 to 11.5	74.7	1.96	[24]
Catfish	Neutralized	−44.3 to 11.4	75.1	1.97	[24]
Catfish	Bleached	−47.1 to 9.9	79.3	1.91	[24]
Catfish	Deodourized	−52.3 to 8	84.3	1.83	[24]
Pollock oil	Unrefined	−69.5 to 14.2	36.9	1.5–3.2	[21]
Red salmon oil	Unrefined	−69.6 to 0.36	40	0.8–1.6	[120]
Pink salmon oil	Unrefined	−64.7 to 20.8	39	1.3–2.3	[120]

ASTM D 97-96a were used for cloud and pour point measurements, respectively. Viscosities of both neat fish biodiesel and blends (B20, B40, B60 and B80) increased with decreasing temperature across all shear rates. Both neat biodiesel and blends followed Newtonian behaviour down to their pour points, and pour points of biodiesel blends decreased with an increase of No. 2 diesel in the blend. In general, cold temperature flow and rheological properties of fish oil improved over conversion to biodiesel.

3.3.5. Oxidation stability

The FFA content and peroxide value are primary indicators of the level of oxidation, and titration is typically used for determination of the FFA content [22,23]. Fourier Transform Infrared Spectroscopy (FTIR) has been used to overcome some of the drawbacks of the titration method and has shown better precision [22,122,123]. Near-Infrared Spectroscopy (NIR) was also used for FFA content measurement for mackerel oil and salmon fillets. Spectrophotometry has been used for measuring ansidine values (secondary oxidation products) [23]. Saponification and conjugated diene values are used as stability indicators of fermented fish by-products [6,23].

The storage temperature, time, and atmosphere affect lipid oxidation and hydrolysis of fish oil [23,31]. Skara et al. has shown that storage at 4 °C and in nitrogen environments inhibits oxidation when compared to higher temperatures under oxygen, as indicated by lower change in ansidine, peroxide and totox values [23]. Peroxide formation at lower temperatures is related to lipid and antioxidant concentration while at higher temperatures it is due to oxygen [124]. Sathivel et al. studied the effect of time and determined that accumulation of peroxides increased after 10 weeks of storage at 24 °C [21]. A study of salmon skin stored over 120 days showed a linear increase in FFA content from 0.6% to 4.5% due to autoxidation [22]. Lipid oxidation of oils recovered from fish liver over storage temperature and time can be higher than other parts due to the active enzymes present [31]. Overall, studies indicate the increase in lipid oxidation with storage time and temperature; however according to Skara et al. other components in the oil mix may inhibit this effect. Skara et al. studied the oxidation of salmon oils over 60 days, in air at 23 °C and did not find high levels of oxidation [23]. This is attributed to the antioxidant effect by the carotenoid content or astaxanthin pigments of salmon oil. Low levels of EPA and DHA, and formation of peptides can also act as antioxidants [6].

Fermentation of visceral oil resulted in slight increase in the peroxide value with no significant change in conjugated diene value [6]. However, there was hydrolysis of lipids to FFA due to lipases present. Fish biodiesel produced through transesterification of marine fish discards studied by Lin et al. had higher initial oxidation stability than waste cooking oil biodiesel or commercial biodiesel due to the higher SFA in fish biodiesel that reduced peroxide formation [119]. As found in the study, with time the stability of fish biodiesel reduced to an extent lower than that of commercial biodiesel (from vegetable oil) due to higher PUFA in fish biodiesel.

3.3.6. Other physical properties (water content, colour and density)

Physical properties such as colour, water content and specific gravity/density have been studied by several authors [e.g. 16,21,32,120]. Sathivel et al. analyzed chemically refined pollock oil using a Minolta Chromameter and determined the colour to be "light yellow" [21]. Similarly, Ivar et al. found hydrolysis of fish waste resulted in clear yellow coloured oil [32]. Crude oil from Japanese fishmeal plants was black in colour [16].

In studies of bulk density the values were 0.902 ± 0.004 g/mL, 0.9 g/mL, 0.81 g/mL and 0.911 g/mL for pollock, red salmon, pink salmon and herring oils, respectively [21,120]. Water content and water activity are measured using aqua lab water activity meters and microwave moisture analyzers. As determined by Sathivel et al., the water activity of pollock, red salmon and pink salmon oils was 0.464, 0.57 and 0.53 respectively [120].

Overall, fish oils have higher viscosity, lower lubricity, more acidity, and higher flash point compared to petroleum diesel. The main concerns raised from earlier research for engines using fish oils were engine deposits in exhaust ducts and increased wear in parts which are constantly in contact with the oil [125]. These are discussed in Section 3.4.1.

3.4. Fish biofuel as a fuel

3.4.1. Crude fish oil

3.4.1.1. Crude fish oil in diesel engines. The UNISEA pollock oil demonstration project used crude fish oil as a blend with No. 2 low sulphur diesel oil in 2.3 MW medium speed two cycle stationary engine generator sets, using pure diesel, 50%, and 100% fish oil blends [125]. Emissions and engine durability were conducted and compared to 100% diesel use. The oil was a by-product from fishmeal plants processing the fish waste. Properties of the oil are compared with other studies as given in Table 16. In general, heat and sulphur contents were lower than for diesel fuels across all blends.

3.4.1.2. Crude fish oil in internal combustion engines. Fairbanks Morse Engine Division of Coltec Industries Inc. tested crude fish oil and its blends with diesel in a medium speed-two cycle-six cylinder type engine [126]. Fish oil derived from pollock oil in surimi plants was used as an alternative to diesel fuel for electricity generation. Fish oil blends were varied between 0% and 100%, at 10% increments in the blend with diesel and tested for performance characteristics, emissions, combustion cycle characteristics, and deposits/wear in engine components at load conditions of 50%, 75% and 100%. Properties of the 100% fish oil are given in Table 16. In comparison to the blends, the pure fish oil had lower volatility. Thermal cracking of the fish oil and blends occurred and the onset temperature of cracking decreased with increase of fish oil in the blend. When compared with 100% diesel, the initial boiling point of all fish oil blends was higher, but pure fish oil boiling point was lower than all blends and pure diesel. The calculated cetane index for measuring ignition delay was not applicable to the fish oil as thermal cracking occurred prior to the mid boiling point. The calculated carbon atomic index as developed by Shell Oil Co. for testing of heavy petroleum fuels proved to be a better method, and the values of fish oil blends and diesel were similar. The lubricity tests carried out using "A Ball on

Table 16
Comparison of fish oil properties from several studies [125–127].

Properties/study	UNISEA	COLTEC	CANMET
Density at 15 °C (kg/m^3)	922.5	923.7	876.9
Calorific value (MJ/kg)	39.4	37.4	40.0
Flash point (°F)	230	331	293
Pour point (°C)	–	−9.4	3
Cloud point (°C)	–	–	3.2
Specific gravity	–	–	0.876
Acid number (mg KOH/g)	–	8.63	–
Kinematic viscosity (cSt)	–	33 (at 38 °C) 22.4 (at 50 °C)	5.42 (at 25 °C) 4.18 (at 40 °C)
Initial boiling point (°F)	–	322	–
Cracking temperature (°F)	–	567	–
Moisture (wt.%)	–	–	0.05
C (wt.%)	–	78.92	77.21
H (wt.%)	–	11.59	12.08
S (wt.%)	0.0084	0.004	0.0034
N (wt.%)	–	–	0.003
O (wt.%)	–	–	10.39
Ash (wt.%)	–	0.0032	<0.001

Three Seats" test showed an increase in wear of the fish oil by a magnitude of 1000 compared with 0.3% diesel fuel.

3.4.1.3. Crude fish oil in combustors/furnaces. Wang et al. carried out a study using Alaskan derived crude fish oil for combustion characteristics of the oil such as emissions and flame stability [127]. Several blends with No. 2 and No. 6 fuel oils were tested for use in boilers and furnaces for heat and/or power generation. Properties of the used crude fish oil are compared in Table 16. The crude fish oil had higher H:C ratios compared to No. 6 fuel oil. Flash and pour points were much higher than both fuel oils, and the calorific value was slightly lower. The kinematic viscosity of fish oil was much lower than No. 6 fuel oil at all temperatures tested, as was the viscosity of blends. The lower viscosity of fish oil reduces the pre-heating requirements and pump demand of the blended oil. In terms of properties such as density, calorific value, kinematic viscosity and C, H, N and ash contents, fish oil was more similar to No. 2 fuel oil.

3.4.2. Fish biodiesel

Ocean Nutrition, which is a division of Clearwater Fine Foods has been producing biodiesel from residual fish oils since 1999 in Nova Scotia [128]. The residual oil is a by-product from omega-3 dietary supplement and functional food production from omega-3 fish oils. The oil is purchased from large scale processors in South America. Part of the produced oil is used for their own energy needs in a boiler and heating system while the rest is distributed through local subcontractors. Biodiesel (fish oil methyl ester) production is 1 million L/year. Biodiesel (fish oil ethyl ester) is also sold by Wilson's fuels for use as home heating oil and/or for blending with transportation fuels [77].

Aquafinca in Honduras operates a plant where biodiesel is produced from fish oil separated from tilapia waste [117] where approximately 8000 t of tilapia waste generated annually is converted to 1.4 million L of biodiesel from the recovered oil. This translates to producing 0.18 L of biodiesel/kg of fish waste. The oil recovery process involves cooking in a boiler and heating to 100 °C, separation of the liquid from the biomass using an expeller, and recovery of the oil from water and residual solids using pre-clarifier. The separated oil is heated, reacted with caustic soda and methanol (20%), and decanted to separate the oil from glycerine to produce biodiesel. The biodiesel is purified through decanting, washing with water vapour at 95 °C, drying, further purification and filtering, prior to sending for storage or pumping/filling stations. The properties of the recovered oil or biodiesel were not given in the study. A life cycle based environmental impact assessment is not still conducted for the process. Issues to be addressed include markets for glycerine, easy access points for obtaining the fish waste, and reliable sources of purchasing methanol and caustic soda.

Steigers Corporation converted 45,425 L of fish oil obtained from processors to 37,854 L of biodiesel with greater than 93% conversion efficiency [129]. Properties of the produced biodiesel were compared with ASTM D6751 biodiesel standards as given in Table 17. Lin et al. investigated oil recovered in the fishmeal industry for biodiesel production [119]. A mix of waste from mackerel, salmon, tuna and cod fish processing was used as the raw material, and the oil was separated by cooking in boiling water, squeezing the liquid, and centrifugation. The recovered oil was brown in colour and contained water, fish residue, saline compounds and other impurities. Oil was purified through absorption by active clay, winterizing at 4 °C, centrifuging, water washing, and finally heating to 105 °C. Transesterification was carried out by using sodium methoxide as the catalyst, and adding methanol at 6:1 ratio (fish oil:methanol). The reaction mixture was homogenized at constant temperature and glycerol separated through gravity settling. The crude biodiesel was distilled to remove the unreacted methanol and further washed with 50 wt.% petroleum ether, followed by distilled water. The lipid content of the crude fish oil was 37 wt.% and increased to 85 wt.% after refining and 92 wt.% after transesterification. Therefore, biodiesel conversion efficiency was 28.9%, and the energy output/input ratio was 5.35. Properties of the biodiesel are compared in Table 17.

A similar study conducted in Taiwan by Lin et al. used discarded parts such as viscera, gills, fins and heads of mackerel, herring and cod for production of biodiesel [130]. The fish oil was obtained by squeezing the fish discards and removing impurities, water and soap through stirring, winterizing (for removal of impurities and components), water washing and centrifuging. The transesterification process used methanol at 1:6 ratio (fish oil:methanol), and 1 wt.% NaOH as the catalyst. Glycerine was removed by gravity settling and centrifuging. Water washing and heating were used to remove unreacted catalyst, methanol, water, volatile compounds and any other impurities. Biodiesel attained in neat form was tested and the results compared with No. 2 ASTM diesel and commercial biodiesel from waste cooking oil. The resulting properties are summarized in Table 17. The carbon residue, viscosity and acidity of the produced fish biodiesel slightly exceed the ASTM specified limits.

Table 17
Comparison of fish biodiesel with biodiesel standards [118,119,129,130].

Fuel properties	ASTM biodiesel	ASTM No. 2 diesel	Steigers (April 2004)	Steigers (April 2005)	Karnataka, India	Taiwan
Specific gravity		0.83	–	–	0.88	0.86
Flash point (°C)	100 min	74	>190	>130	176	103
Calorific value (MJ/kg)		46.2	–	–	42.2	41.4
Water and sediment (vol.%)	0.050 max	–	0.40	0.00	–	–
Carbon residue (wt.%)	0.05 max	1.57	0.05	0.022	–	0.76
Sulphated ash (wt.%)	0.020 max		0.021	0.000	–	
Viscosity at 40 °C (cSt)	1.9–6.5	3.4	4.4	4.3	4.0	7.2
Cetane	40 min	53.2	49.4	51.9	–	50.9
Cloud point (°C)	3 °C	–	−1.0	−1.0	–	–
Copper corrosion	3B max	–	1B	1B	–	–
Total acid number (mg KOH/g)	0.80 max	–	0.14	0.39	–	1.17
Free glycerine (wt.%)	0.02 max	–	0.001	0.006	–	–
Total glycerine (wt.%)	0.24 max	–	0.19	0.167	–	–
Distillation (atmos. equiv. 90% recovered)	360 °C max	–	379 °C	380 °C	–	–
P (wt.%)	0.001 max	–	0.0057	0.000	–	–
O (wt.%)	–	0	–	–	10.9	7.19
C (wt.%)	–	87.17	–	–	–	80.01
H (wt.%)	–	12.76	–	–	–	12.75
N (wt.%)	–	0.07	–	–	–	0.05
S (wt.%)	0.05 max		0.00023	0.00010	–	

Table 18
Process parameters and products of biogas from fish waste [57,132–137].

Seafood effluent	Type of reactor/reaction	Product	Other gases	References
Blue crab cooking wastewater	Anaerobic digestion	6.6–10 L/L of feed, CH_4 – 68%	CO_2 – 28% and H_2S – 1.5%	[132]
Crab residues	Leach bed reactor + hybrid sludge-bed filter	>70% of product was biogas		[133]
Fish offal with cattle slurry	Batch codigestion	47.3–31.1% volatile solids reduction		[134]
Canning sardines and tuna	Upflow anaerobic sludge blanket	CH_4 – 0.23 L/g		[135]
Tuna processing liquid effluent	Anaerobic cylindrical fixed bed reactor	0.18 m^3 CH_4/kg volatile solids degraded		[136]
Fishmeal processing effluent	Anaerobic filter	0.05–2 L/g COD		[137]

Godiganur et al. analyzed engine performance and emission characteristics of fish biodiesel and its blends in India, and it was of transparent light yellow colour without any suspended matter [118]. The biodiesel has been obtained from manufacturers and suppliers of biodiesel (karanja and mahua oil) to TATA motors and the process details are not given. Properties of the fish biodiesel are compared to other fuels in Table 17.

Other developments in biodiesel production from fish waste include ENERFISH project in Finland in partnership with Vietnam, plans for production of biodiesel from fish fat recovered from wastewater by the National Technological Centre for Canning of Fish Products in Spain, and feasibility study conducted by the Sustainable Community Enterprises in Vancouver for converting fish oil to biodiesel [117]. While the 2005 feasibility study conducted by the Sustainable Community Enterprises (Vancouver) showed that biodiesel from fish oil is not economically viable, the 2007 study proposed a base transesterification system or a fully automated acid/base two stage systems equipped with a water wash as viable.

There are small differences between the fish biodiesel properties due to fish feedstock and processing parameters among other factors. However, most properties of marine biodiesel are close to the values of No. 2 diesel. The high elemental oxygen content and slightly lower carbon residue associated with fish oils translate to better combustion properties and lower particle emissions. A potential drawback particularly in cold climates is the high viscosities associated with pure biodiesel and blends, when compared to diesel. In comparison to the crude fish oil properties discussed in earlier sections, improvements are seen after conversion to a biodiesel. Another challenge in biodiesel production via transesterification remains the produced glycerol which according to Boyd et al. has a limited market due to other glycerol sources [7].

3.4.3. Biogas from fish waste

Biogas is derived from fish oil or the waste itself and typically produced by anaerobic digestion [57]. A system used for rainbow trout processing plan effluents consisted of a digester connected to a sedimentation column with an aerobic filter, and final polishing using a Zeolite column. The digester reduced the total, soluble, suspended, and volatile solids and the zeolite column reduced total nitrogen and wastewater contaminants.

Salmon hatchery sludge containing 1.5–3.3% solids, 32% N, 8.5% P and low heavy metals was treated through anaerobic digestion to produce biogas [57]. The low ash and high moisture contents of fish waste were beneficial in biogas production. Bio-gas was produced from waste of fish oil/fishmeal, fish filleting, herring cannery, mackerel cannery, shell fish and smoke fish industries by using both anaerobic digestion and codigestion. Reactor failure occurred at loading rates of 2 g VS/L/day and higher when co-digesting with fish and wood wastes, due to the high level of long chain fatty acids in fish waste. Results obtained from other biogas studies are summarized in Table 18. Factors inhibiting biogas production from fish waste were presence of high concentrations of different ions and high levels of sodium in the waste [57,131].

3.4.4. Fish biofuels from other processes

Properties of the ozone treated fish oil in Murakami et al. are summarized in Table 19. The product was compared to biodiesel produced via transesterification using a methanol and NaOH system; by-products included 10 wt.% glycerine and 50 wt.% wastewater [76]. The ozone process also resulted in a better quality biodiesel with fewer odours, no glycerine, less waste and was associated with lower chemical use. The ozone produced biodiesel had similar or higher, heating values compared to petroleum diesel and the pour point and flash point values were lower than those of petroleum diesel.

Pyrolysis has also been investigated for conversion of fish oil. Meier et al. used a continuous fast pyrolysis plant to thermally crack waste fish oil [74]. The waste fish oil was pre-treated using aerobic treatment followed by centrifugal separation, and fed to the pyrolysis unit as an emulsion with water. The waste fish oil converted to 15.85% gas, 11.32% coke, 2.14% solids, and approximately 73% of bio-oil which separated by gravity from the aqueous phase. The bio-oil consisted of light fraction in the C4–C10 range, heavy fraction in the C11–C22 range and an oily sludge, and was distilled under atmospheric conditions to obtain purified products in boiling ranges of gasoline and diesel. Pyrolysis and distillation resulted in a reductions of density, 56% sulphur, and 26.7% IV (due reduction in unsaturated HC) when compared to the waste fish oil. However, the water content (due to addition of water) and acid value (due to high carboxylic acid contents) increased. The light

Table 19
Properties of fish biofuels produced by ozone treatment and pyrolysis [74,76].

Property	Ozone treated fish oil	Pyrolyzed fish oil		
		Bio-oil	Light bio-oil	Heavy bio-oil
Water content (wt.%)	–	0.68	0.06	0.04
Sulphur content (wt.%)	–	0.01	0.02	0.01
Soot (wt.%)	0	–	–	–
Acid index (mg KOH/g)	–	131.1	107.3	142.5
Iodine index (cg I_2/g)	–	64	98	67
Cold filter plugging point (°C)	–	–	–	14
Kinematic viscosity at 40 °C (cSt)	131	–	–	4.8
Flash point (°C)	38	–	–	31.5
Pour point (°C)	−16	–	–	–
Density (kg/m^3)	870	896.5	835.9	886.6
High heating value (MJ/kg)	44.8	–	–	–

bio-oil was 22.63% of waste oil and 31.07% of pyrolyzed oil after distillation. In comparison to pyrolyzed bio-oil, the light bio-oil had lower density and water content, similar acid values, and higher degree of unsaturation (52.56% higher), and also lower C4–C8 and higher C9–C12 compounds than gasoline. The heavy oil was 54.25% from the pyrolyzed oil and 39.52% from waste fish oil, and had low water content, IV and high acid values than bio-oil. Compared with Brazilian diesel specifications the heavy bio-oil fraction had higher CFPP and density and a lower cetane index. The heavy oil also had lower volatility and higher C4–C12 and C20–C22 contents than petroleum diesel. Both light and heavy bio-oil fractions had lower sulphur values. Properties of the bio-oil fractions are compared in Table 19.

3.5. Engine performance and emissions of fish biofuels

3.5.1. Engine performance of crude fish oil

In the UNISEA demonstration project, wearing in fuel injector or engine-mounted fuel pumps and hard deposits in exhaust component (piston ring seating grooves, exhaust ports, exhaust turbine inlet rings) were not observed in the stationary diesel engine [125]. However, higher than normal suspended in-soluble protein content in the fish oil increased load on fuel purifiers and filters. Start-up of engines was better than with diesel fuel and no difficulties occurred in engine shut downs. An increase in the engine's fuel rack position and engine-mounted fuel filter pressure differentials were observed due to lower thermal content and higher viscosity. The engine's crankcase lubricating oil was tested at 24 h intervals and did not show contamination or unusual consumption rates. Adverse effects during storage at cold winter conditions were prevented by re-circulating the fish oil using a heater-equipped centrifugal fuel purifier. There are limits to the application of the test results of the study due to the rare engine design used. Suggestions made for improvement are inline blending as a substitute to batch blending, and pre-purification of fish oil before use by the installation of dedicated fish oil centrifugal fuel purifiers and/or suitable filtration equipment. The latter is to avoid entrained water and suspended non-soluble protein from creating undesirable conditions in diesel engines.

Engine performance tests conducted in the Coltec study, for a medium speed internal combustion engine showed an increase in specific fuel consumption with the increasing fish oil in blend, across all load settings [126]. This was attributed to lower heating value of fish oil. At 100% load setting the thermal efficiency increased with increased fish oil in blend. Combustion cycle analysis tests did not show differences between ignition delay characteristics of fish oil blends and neat diesel. Combustion pressure and heat release were also not different. Inspection of engine components after 37 h of operation showed increased levels of deposits on the upper piston section, which was higher than the lower piston section. This difference is attributed to cooler surfaces of the upper piston compared with the lower piston. During the short duration of testing, severe deposits or wear was not reported. Transesterification of the crude oil is proposed to reduce deposits. Overall, except for the slight increase in deposits, fish oil and blends have demonstrated similar ignition qualities and excellent combustion characteristics compared to diesel fuel.

Testing for use as furnace oil in the CANMET study suggests fish oil as a better substitute for No. 2 fuel oil due to the ability to create similar thermal effects [127]. Fish oil and 5% and 10% fish oil blends in two types of oil fired residential boilers (30 kW and 150 kW) were carried out with no adverse effects. Higher viscosities are not a concern for these applications; therefore, straight run fish oil can be used in combustors without any further purification/refining or transesterification greatly reducing the cost. Suggestion for better use of the oil is removal of impurities such as proteins, waxes and water that cause adverse conditions in engines and during storage.

3.5.2. Engine performance of fish biodiesel and blends

Halifax Regional Municipality Metro transit bus system tested fish biodiesel or fish oil ethyl esters between November 2003 and March 2004 [77]. Fish biodiesel blends (with petroleum diesel) of B20 in Metrobus transit fleets and B100 in municipal buildings are promoted by the Municipality. However, use of B100 was difficult due to clogging of engine filters, issues associated with pumping from fuel tanks to engines and burners, and gelling at temperature of 3 °C.

Steigers Corporation tested fish biodiesel-B100 in a generator including B20 and B40 splash blends in utility vehicles [129]. Excellent efficiency and operability as well as material compatibility with generator engines were reported. The blend-B100 was tested for 48 h in a test bed engine or generator. Better efficiency and operation and lubricity gains were observed, however, injector deposits occurred. Protein fouling occurred in engine fuel filters as well as injector deposits and was attributed to the presence of protein in feedstock. Filtering of fish biodiesel is proposed to reduce deposits.

Fish biodiesel (fish oil methyl ester) was tested in Karnataka, India, in a four stroke-three cylinder-air cooled direct injection diesel engine at a constant speed and varying load conditions [118]. Fish biodiesel blends of 0, 10, 20, 40, 60 and 80% (v/v) with neat diesel were used to analyze engine performance indicators; brake specific fuel consumption, brake specific energy consumption, thermal efficiency and exhaust gas temperature. The observations are summarized in Table 20.

Fish biodiesel was tested in Taiwan in a direct injection, four-cylinder, four-stroke diesel engine at constant torque and speeds varying from 800 to 2000 rpm [130]. The presence of PUFA in fish biodiesel improved cold temperature properties such as CFPP and fluidity, thus improving the issues with sticking, freezing and stalling of vehicles. Increases in brake power output and exhaust gas temperature occurred for B100. Higher oxygen content in fish biodiesel resulted in lower exhaust gas temperature and shorter combustion duration times compared with diesel. To achieve the same energy output, the fuel consumption rate of fish biodiesel was higher than No. 2 diesel and lower than waste cooking biodiesel. Brake fuel conversion efficiency (engine power output:heat release rate ratio) was higher for fish biodiesel than No. 2 diesel at engine speeds less than 1400 rpm, however lower beyond this speed, and is attributed to higher oxygen content. The "oxygen-rich advantage" decreased with increase in mixing extent in the combustion

Table 20
Engine performance results of fish biodiesel [118].

Property	Observations
Brake specific fuel consumption	- Increased with percentage fish oil in blend, due to lower calorific values of biodiesel than petroleum diesel - Higher for 100% biodiesel than 100% diesel - Higher mass injections for biodiesel blends than diesel for the same volume and pressure of injection (due to higher density of blends than diesel)
Brake specific energy consumption	- Minimal value obtained for B20 and lower than that of diesel - Higher for B40, B60 and B80 than diesel due to lower calorific values
Thermal efficiency	Maximum attained for B20, higher than that of diesel
Exhaust gas temperature	- Increased with biodiesel percentage in blend - Higher in biodiesel blends than diesel, due to higher heat loss in blends

Table 21
Percentage reductions in-use emissions in engines.

Source	[127]		[127]	[125]	
Type of engine	Furnace		Residential boiler	Stationary diesel engine	
Petroleum fuel	No. 2 fuel oil		No. 2 fuel oil	No. 2 low sulphur diesel	
Blend	50% fish oil	100% fish oil	5% fish oil	50% fish oil	100% fish oil
CO_2	4%	4%	0%	5%	6%
CO	−6%	−25%	2%	−18–2%	−28–2%
PM	–	–	–	35–43%	43–63%
SO_2	−40%	−96%	−4%	−40%	−80%
NOx	(NO) 11%	14%	−1%	4–6%	6–7%

Table 22
Fat content and recoverability of fish discards of NL [31].

Type of fish discards	Year	Estimated fish processing discards (kg)	Fat content (wt.%)	Assumed oil recoverability (kg)
Capelin	2005	3,372,100	3.80	96,105
Herring	2004	8,335,680	9.04	565,158
Mackerel	2004	2,362,724	13.89	246,136
Seal blubber	2005	8,999,301	87.70	7,892,387
Farmed salmanoids (Atlantic and Steelhead)	2005	205,670	23.00	155,147

chamber. Equivalence ratio measured in terms of residual oxygen in the exhaust gas was lower for fish biodiesel than No. 2 diesel.

In other studies, fish biodiesel was tested in a single cylinder diesel engine and achieved a maximum power output 3% higher than using neat diesel [118]. Lubricity gains were reported in another study when used in blends indicating the potential use of fish oil blends as an additive [7]. Fish biodiesel produced through ozone treatment was tested in a Japanese automobile (103 kW at 3200 min^{-1}) without any engine modification. Compared to vegetable biodiesel, ozone treated fish biodiesel had better fuel properties [76]. A 3 h engine test conducted at full loads for horse power outputs of 40%, 60% and 100%, did not indicate to engine issues. In general, heavy duty medium speed diesel engines show better performance with the use of low cost liquid biofuels such as waste oils/biodiesels [118].

3.6. Emissions from fish biofuels

The in-use emission reduction by substitution of fish biofuels and blends with No. 2 low sulphur diesel fuel and No. 2 fuel oil in stationary diesel engines, furnaces and boilers is summarized in Table 21.

In the UNISEA fish oil demonstration project, emissions were measured for CO, NO_x, CO_2, and PM, and SO_2 emissions were estimated from fuel sulphur content [125]. Overall, maximum reductions were in pure fish oil use and were up to 63% of PM, 28% of CO and 80% of SO_2 emissions. There were slight increases (<6%) in both NO_x and CO_2 emissions. For the environment in which the powerhouse operated the main concern was SO_2, thus operating with fish oil blends was more beneficial even with the increment in NO_x emissions. The study conducted by Coltec showed slight increases in NO_x and CO_2 emissions, with increasing fish oil in blend when compared to pure No. 2 fuel oil use [127]. The residential boiler study showed an increase in CO emissions while other emission types decreased. As given in the study, other than NO (in furnace) and NO_x (in residential boiler), emissions during pure fish oil use were lower than pure No. 6 fuel oil use. Increase in NO_x emissions with the increase of fish oil in the blends is due to lower volatility of the fish oil and formation due to nitrogen in the air.

Ozone treated fish biodiesel showed negligible SO_2 and lower soot and particulate emissions compared to petroleum diesel, in Japanese automobiles [76]. This is due to lower molecular weight fractions and higher oxygen content in fish oil compared with petroleum diesel. Overall, improvements in fish biofuel properties are needed for substitution of No. 2 diesel oil. However, crude fish oil can better replace combustor fuels without any engine modifications. In addition, reductions in CO_2, CO, SO_2, PM emissions and increments in NO_x emissions have been observed.

3.7. Remote plants: Newfoundland and Labrador as a case study

The fish processing industry is an important part of rural and remote communities in Atlantic Canada and generates approximately 418,000 t of waste per year [98]. In NL alone 35,000 t of fish waste is generated annually. Four primary types of fish are commercially processed; ground fish (cod, flatfishes, Greenland product), pelagic/fin fish (capelin and herring), shell fish (shrimp, crab, and clams/quauhaug) and miscellaneous (lumpfish roe and seal) [89]. By 2002, 131 facilities were in operation registered under the act; five of which were aquaculture facilities.

Fishmeal plants (2 sites) and seal processing plants (1 site) are required by the provincial law to obtain a certificate of approval under the environmental protection act [89]. Screening is the most common type of treatment, where most settleable solids are collected for disposal or fishmeal processing. Discharge of fish offal at sea and land waste sites is approved for NL processors due to the remote location and unavailability of facilities for fish oil or meal processing. However, regulations may become stringent in the future requiring better waste management practices.

In NL, by-product recovery is minimal due to the remoteness, high costs, and high moisture content [31]. Capelin, mackerel, farmed salmanoid, seal blubber and unutilized herring discards are either used as bait or as animal feed in some plants. Part of the capelin and seal blubber discards is sold to foreign food grade markets. With only a few fishmeal plants in operation, oil recovery is minimal. Oil recoverability of fish discards of species processed in NL was estimated by a study for Environment Canada as given in Table 22. Fat content by weight of species and assumed percentage recoverability of 80% were the basis for the estimation, and varied between a low value of 3% to a high value of 23%. With an 80% recovery this translated to about 965 t/year of oil in the waste. However, presently, only 5% of herring oil is recovered.

High FFA content, heterogeneity of the waste and remoteness mean processing to recover edible oils or recovery of oil for export as a biofuel would likely not be feasible. Onsite processing and use as a fuel blend for applications requiring low quality oils would

likely create economic benefits due to energy savings and reduced costs in disposal. Use in boiler and furnace in plants, home heating oil in the community or even fish processing vessels are some of the possible applications.

4. Conclusions

Waste oils from processing of greases and animal fats can be used to derive biofuels for direct use in applications where high quality fuel is not required and/or the engine is flexible to accommodate lower quality oils. Purification, blending with petroleum fuels, refining to biodiesel and other forms are options for improving recovered oil properties. Transesterification is the typical method of refining commercially, while pyrolysis, microemulsification, ozone treatment and hydro-processing have been tested at lab scale. Overall, waste oil derived biofuels are advantages over conventional petroleum based fuels; in that waste or a by-product from a processing plant is used instead of disposed, overall lowering GHG emissions and most other toxins (excluding nitrogen oxides) over life cycle of fuel production, use and disposal.

In areas of substantial fish processing, on-site processing of oil to fuel from fish waste for use on-site or in the community can result in environmental and economic benefits, especially where processing plants are remotely located. Fish processing plant effluents are heterogeneous in composition and the lipid and TAG content vary depending on the type of fish, discarded part, season of harvest and processing techniques. In addition, due to the high PUFA content and active enzymes present, the waste has low thermal and oxidation stability requiring special attention in storage and transport. The key challenge to the feasibility of use of the fish oil as a fuel is recovery of the oil from the waste. If a fishmeal plant is present then the recovered oil is typically of high enough quality to use in plant operations (e.g. utilities or large engines). Crude fish oils have been used as a partial and/or full substitute for No. 2 diesel and No. 2/No. 6 fuel oil in existing stationary diesel engines and combustors (furnaces, boilers) with good results. The main advantage has been reductions in emissions and cost savings in fuel consumption; the specific fuel consumption, viscosity, density and cold flow properties were improved by blending as much as 50 wt.% with petroleum fuels. Long term use of crude fish oil blends in these engines and boilers may prove feasible when the fish oils are purified using simple techniques such as filtration to reduce sediments, proteins, and other impurities. However, fishmeal plants are not typically present in remote communities and therefore other options for economically recovering the oil are required. These options must be easily incorporated into the existing infrastructure and operationally straightforward to be successful. Refined fish biofuels, through transesterification or other process, can improve the quality and therefore expand the application of the fuel.

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